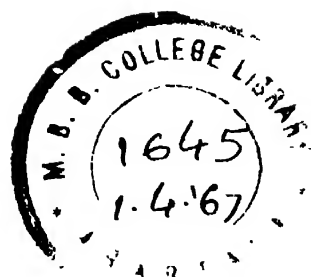


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# ERRATA

Page.	Line.	Read	for
62	31	$T_{\infty}-T_c$	$T_c-T_{\infty}$
122	19	(III) as...	(II) as...
123	1	$C_{18}H_{14}O_2N$	$C_{18}N_{15}O_2N$
398	5	$K_i$	$K_1$
398	7	$RM^*_{11}$	$RM$
400	1	$-K_{t_2} [R] [M^*]$	$-K_t [R] [M^*]$
400	14	tetraphenylsuccinonitrile	tetrephenylsuccinonitrite
401	last line of the table	Sp. viscosity	$\mu_{sp}$
402	10	$[M_r]$	$M$
402	eq. (8)	$e^{-\frac{(r-2) k_1^{\frac{1}{2}} c_1^{\frac{1}{2}}}{[M]}}$	$e^{-\frac{(r-2) k_1^{\frac{1}{2}} c_1^{\frac{1}{2}}}{M}}$
404	1	$\frac{d [M_r]}{dt}$	$\frac{d M_r}{dt}$
551	31-32	(found : Cl, 22.2 ; Br, 34.5...)	(found : Cl, 21.6 ; Br, 36.3...)



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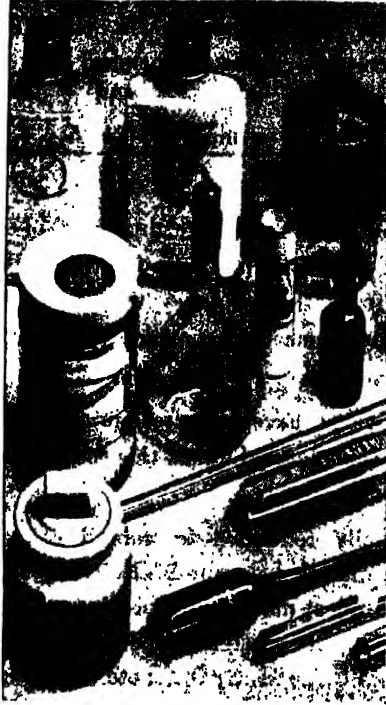
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For & on behalf of the Trustees:

K. N. BAGCHI

F.R.I.C., F.N.I.

General Secretary,

Royal Asiatic Society of Bengal.

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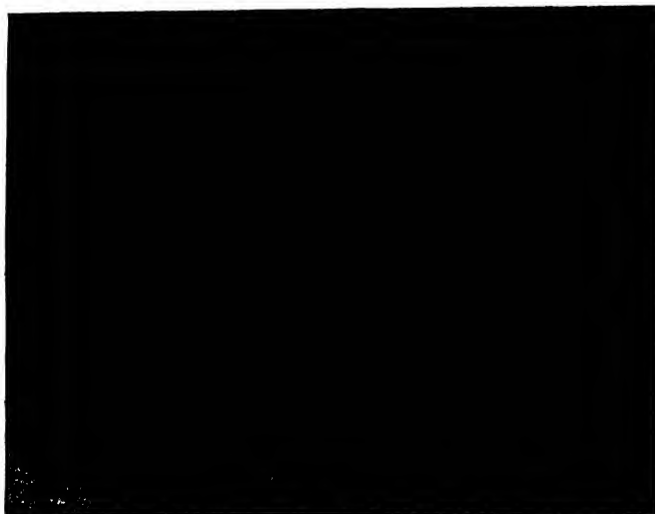
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# THE SILVER JUBILEE ADDRESS

By The President of the Society, PROFESSOR P. RÂY, M.A., F.N.I.

The occasion of a birth-day or a jubilee observance for an individual or a society is obviously one of rejoicing ; and more so in the case of societies where it is not mingled, unlike in that of individuals, with the disturbing thought of an approaching decay with age, followed ultimately by an inevitable physical annihilation. But it is also an occasion for retrospect and recollection, that permit us from a review of our past achievements and failures to discuss how best we can design the pattern of our future in order to fulfil the aims and objects of our Society.

The aims and objects of a learned society like ours are primarily to encourage and foster the spirit of enquiry and original research through exchange of ideas and informations between workers in the same field all over the world ; to protect and develop the scientific life in our own country so far as the study of chemistry is concerned ; to promote the growth of a cultural fellowship among the chemists in general. Looking back upon the past twenty-five years of our existence and making a dispassionate analysis of our achievements and activities, we can discover little justification for complacency or gratification. The standard of our publications has failed to reach the level which we might have not unreasonably expected from the number of workers in various universities and research institutions of our land. There was a time in the distant past of India's history when she enjoyed the distinction of being the torch-bearer of knowledge, both as regards the theories and practice of chemistry, simultaneously with, or in some respects as the historians suggest, earlier than, her sister-nations in Babylonia, Mesopotamia, Egypt, Greece, Arabia, Persia and China. Then with the loss of her freedom there came a dark age in her history, when she lapsed into a complete intellectual inactivity with absolutely no noteworthy record of her contribution in experimental sciences for several centuries. After the advent of the British and her contact with the West, India gradually revived her interest in scientific pursuit with the establishment of universities and provision for teaching in experimental sciences. So far as our own branch of science, chemistry, is concerned, a short history of our activities up to the present time has been presented in the Jubilee brochure. These, as I have just remarked, have not been of the order that might inspire confidence in a better or brighter future. Now that India has regained her freedom, it should be the bounden duty of all those of her sons, who devote themselves to the pursuit of science, not to spare any efforts so that she may once again make her own contribution to the world's stock of knowledge and claim her rightful position in the cultural and scientific confraternity of nations.

It will not, therefore, be out of place to discuss here the nature of our present shortcomings and imperfections, and to suggest what appears to me the possible remedies for the same. It may generally be stated without fear of contradiction that the basic scientific training in our schools and colleges is far below the standard aimed at, with the result that the students joining the post-graduate classes of the university, are

usually ill-equipped for an advanced course of study, to be followed by a training in research work. So, unless the feeder institutions imparting training to the undergraduate and graduate classes are improved, it is idle to expect better finished products from the university. However much we may try we shall never be able to build a pyramid upon its apex. An imposing castle can never rest upon a loose foundation. It is well known that the training in our schools and colleges are imparted on a mass scale, and these institutions are mostly run on a commercial basis, with ill-equipped laboratories, by a body of ill-paid, discontented and inefficient teachers. This dearth of qualified and properly trained teachers can be attributed not only to unattractive emoluments, but mainly to the simple reason that bad materials are never known to yield good products. For, students of today become teachers of tomorrow. This does not of course necessarily mean that there are no exceptions. But we are concerned here only with the average. The entire system thus gets vitiated through the perpetuation of a vicious cycle. It is a happy augury that with the establishment of the National Government the State has realized the importance of science in the planning of national welfare and national reconstruction, and is ready to help the universities with financial assistance for a regular supply of trained personnel and research workers. Both the Government and the public have now appreciated the policy of supporting scientific research as a national investment. For the reasons set forth above, such support to be effective should, however, be distributed in a co-ordinated manner not only to improve the post-graduate and research trainings in the universities, but also to strengthen the basic scientific education in the schools and colleges. For, a tree cannot be made to bloom and yield fruits unless it draws nourishment through its roots. Moreover, the universities and research institutions too suffer likewise from a dearth of capable and inspiring teachers and investigators, though, fortunately, most of their laboratories are more or less fairly well-equipped. The situation in this respect has been growing increasingly worse, as the few talented scientists, that the country could be said to possess, are being persuaded to leave the universities and research institutions for administrative, planning and organizational work under the Government. If science be deprived of the teachers and workers of creative gift and inspiring contact, whose influence and examples are sorely needed to guide the younger generation in the universities and colleges, science will never be able to grow. It might be said that many eminent scientists in U.S.A. and U.K. are engaged in administrative services of the State, devoted to planning, organization, supplies, publicity and information. But it should be remembered that India is not in a position to imitate U.S.A. or U.K., whose resources in material and gifted scientific personnel bear no comparison with those of India. The number of really capable scientists in India is too limited for her to spare any of them, without serious consequences to the progress of Indian science, for services other than that of teaching and research.

I have just dealt with one of the factors calculated to hamper the progress and development of science, and particularly of chemistry in India. Another one, which to my mind is of no less significance and contributes to the same end, lies in the tendency, generally noticeable among the members of the public as well as among the more enlightened quarters including a large body of the scientists themselves,

to entertain a confounding conception regarding the relative importance of fundamental knowledge and its practical application. The people are generally inclined to think that the material fruits of the application of science can be enjoyed without the cultivation of science itself. This is something like expecting a quick and increased return from a trade without adding to its capital. There can be no short cut to applied sciences with material benefits except through the thorough training in pure sciences. Sowing and reaping cannot go together. Attempts to train personnel in the practical application of science on a background of imperfect education of basic or pure science can only give rise to a band of mechanical scientific workers, who will at most be able to mend what we have, but not to build what we want. It is therefore, inexplicable why this simple logic that a sound education in pure science should precede that of applied science is not readily recognized, except for the fact that the lure of ready profit and quick return is a stronger force than reason in human nature. But any attempt to invert the order can lead us nowhere, like putting the cart before the horse. As a member of the Selection Committee for appointment of lecturers for Government Colleges, on many an occasion I have had personal experience of the influence of such misconception on the part of the authorities concerned. A candidate with a degree in applied chemistry is generally preferred to one with a degree in pure chemistry, though somewhat better qualified from a consideration of his fundamental knowledge. Of the two candidates, for instance, one who has carried out some work on the extraction of citric acid from lemon, or tartaric acid from tamarind, or on the use of Bidyadhari (a river in Bengal) silt for making indigenous pottery, in none of which there is anything particularly new either in knowledge or technique, generally finds preference to one engaged in some research work, say, on the chemistry of hormones, sterols or bile acids. The reason advanced is, what is the use of trying to synthesise, or solve the constitution of a complicated organic substance, or of measuring the length and breadth of a molecule, unless it has got some profitable practical application. Science could never have grown if utility or a profit motive would have guided the labours of its investigators, or money would have been a measure of scientific knowledge. Chemistry would then have remained buried for all the time in the dark periods of alchemy. On the other hand, this should under no circumstances be taken to mean any discouragement to the application of science. For science, without application, would have remained in aristocratic isolation merely as an intellectual luxury or curiosity for the few, and would never have been able to make any contribution to the progress of humanity and to the alleviation of human suffering. What is really needed is a harmonious and orderly development of the two in their proper relationship. For, it is recognized that science is both knowledge and control. New application may often advance theoretical knowledge as much as new theory lays the basis for application.

In consequence of this inordinate predilection to researches made to order, obviously born of the exigencies of war condition, but continued and encouraged even now on the plea of planning for development, there has been a general decline in the freedom of thinking, without which there cannot be any real advancement of fundamental knowledge. This has also contributed in no small measure to retard research activities in pure science. If, therefore, India is to take her rightful position in the world of science and render

useful service to humanity, she cannot afford to ignore the cultivation of pure science.

No useful purpose can be served here by entering into a discussion about the ultimate object of science, which usually finds expression in two alternative forms viz., the advancement of pure knowledge or of material benefits to mankind. But it is indeed paradoxical that the greatest threat to the material welfare of men in this world arises from the practical application of science itself. The last two global wars furnish an unmistakable evidence to this end. What an unprecedented and colossal destruction of human lives and properties was wrought by the last world war, what enormous and staggering waste of materials and money had to be borne for its preparation and prosecution, what widespread and untold misery and suffering, scarcity and starvation it has brought for the wounded and bleeding humanity, what dreadful poison of intense bitterness, hatred, conflict and moral degradation it has scattered over all lands, are too apparent to need any recounting today. It cannot be denied that this has all been possible through the practical application of scientific knowledge. Applied science has placed in the hands of man an immense power which he can employ either to satisfy his passions and prejudices, his lust for position and greed for wealth, or to serve the humanity at large. But forces of egoism, pride and passions in this world often get stronger than those of charity, sympathy and service, and lead to the abuse of power generated by the application of science. Need is, therefore, keenly felt today for a reorientation of applied science and its utilization for serving the fundamental human needs and advancing the causes of human welfare. It should ban and discard all researches on the production of increasingly more powerful super-weapons and ammunitions of war, and confine itself rigidly to the problems of food and nutrition, health and diseases, houses and shelter, clothings and apparels, travels and transports, and in the production of cheap power that might be utilized equally by all to meet their primary requirements. It is high time that science should direct its efforts to improve the condition of man himself, relating to his body and mind, in preference to that of his environment, which has been, more or less, its exclusive pursuit so long. The result is that there has been a marvellous improvement in the material and external conditions of man's life, but he has not been able to fit himself properly into these. He has released power from the material atom, which he fails to control with the power of his mind. This was more or less the reply which the Council of the Indian Chemical Society gave to the appeal addressed to them by the Committee for Foreign Correspondents of the Federation of American Scientists on the subject of international control of atomic energy. The Council of our Society pointed out that as the scientists themselves cannot disown their responsibility in the production of atomic bombs and other dreadful weapons of destruction, they should first direct their attention to reform their own selves before trying to mend the world at large. If the scientists fail to keep their own house in order, they will forfeit all right to educate the public opinion of the world. The Council of the Society, therefore, rightly suggested that the scientists of the world should organize themselves into an International Federation, every member of which should pledge himself that he will completely non-cooperate with all activities connected with preparation of war, or with exploitation and enslavement of

human beings, and that he will be prepared to undergo willingly all possible persecutions and sacrifices for this noble cause. In a word, science must not be allowed to become a victim of its technologists, as religion has often become the victim of its fanatics.

We, the chemists of India, besides making our humble adventures into the vast field of fundamental knowledge of chemical science, can profitably direct our attention to numerous practical problems of particular significance to our country, and of which facilities for investigation are readily available. A few of these may be mentioned here by way of illustration. India is known to be rich in mineral matters and vegetable products. She also exports a considerable amount of certain animal products of great technical value. These provide a wide field of fruitful investigation by the students of applied chemistry.

Of the mineral matters, India possesses rich deposits of iron, manganese, aluminium and chromium ores. She has also got a vast deposit of monazite sand, the richest in the world in its thorium content. There is also a limited deposit of copper ores in India. Among the other important minerals, which India may be said to possess in fair abundance, mention may be made of magnesite, lime-stone, marble, ilmenite, gypsum. Mica is another important mineral of which India is a major supplier for the world. Proper and economical working up of all these mineral resources to supply India's need and to add to her wealth will make a great demand on the practical application of scientific knowledge of her chemists.

Coal is another important mineral with which India may be said to be well supplied. A large number of important industries dealing with solvents, disinfectants, synthetic dyes, perfumes, drugs and liquid fuels, which are based upon its utilization, are awaiting development in India.

Industries dealing with silicates and refractories, particularly the glass and ceramics, are practically in their infant stage in India; and there is a great demand for their rapid extension and development.

India's wealth of plant products places her in a position of great advantage. From these she can obtain alkaloids, sugars, oils, fats, waxes, resins, gums, cotton, essential oils, etc. Her wood, bamboos and grass are also being utilized for the production of paper pulp. Many other subsidiary industries of considerable economic value may also be evolved from them.

Among animal matters, bone and hide are the two most important materials of which India has a plentiful supply. These have not been sufficiently utilized till now.

But in addition to these problems of common knowledge, which have long been before the Government, industrialists and scientists, I would like to refer here particularly to a few others which are of primary importance for the health and well-being of the people, and to which little attention is often paid by us.

India is suffering from a serious scarcity of foodstuffs for a pretty long time, and the Government is advocating urgent measures for increased production by introduction of artificial fertilizers and improved methods of agriculture. But we do not seem to attach due importance to the safety and preservation of the crops before and after these are

harvested. It has been shown that about 3-5 percentage of the world's annual food production, particularly of cereals and oil seeds, are lost due to attack by insects, fungus and rodents. This loss is, however, distributed unevenly over different countries, depending on climatic conditions and preventive measures employed. It is said that in East Africa this loss of foodstuffs amounts to nearly 30 percentage of their total production. I am afraid, the loss in India would be no less, considering its geographical position, climatic condition, and its failure to adopt proper and scientific measures to minimise the loss. Researches aimed at the production of new and powerful insecticides, otherwise harmless enough to man and animals, and also at the development of methods which would ensure the safe storage of the grains, free from any fungoid growth, should engage the serious attention and efforts of our workers.

Then again, there are very few places in India, which are not infested with mosquitoes and flies. Mosquitoes are not only an intolerable nuisance, but some species of them are positively dangerous to men and animals, being carriers of malaria, filaria, kala-azar and other diseases. So are the flies and fleas. Measures for their extermination and control should necessarily constitute an important item in the scheme of our national development. This also offers a field where the chemists can render valuable services.

There is another formidable pest in the form of water-hyacinth, which is particularly characteristic of Bengal and Assam. It has become a great impediment to agriculture and river communication in those parts of the country. No adequate measure has yet been devised to eradicate this pest. Development of some chemical methods for their extermination, or for inhibiting their growth and propagation, presents a very suitable subject of research.

Finally, the utilization of many waste vegetable matter, such as bagasse, straw, coconut shells and fibres, jute-plant stalk, etc., which by suitable chemical treatment might give rise to useful products in the form of cheap building and clothing materials, also comes under this category and deserves a close and persistent study by the workers in applied chemistry.

In India today we need an intensive pursuit of science not only for the development of numerous resources of the country with a view to raising the standard of living of the people who are proverbially poor, but also to make her own contribution in advancing the bounds of human knowledge. I need not dwell here on India's achievements in the remote past, when she excelled many of her contemporaneous nations in arts, literature, philosophies, architecture and mathematics, and even in practical sciences like astronomy, medicine and chemistry. But we shall do well to recognize today that further advancement of human knowledge can only be made through the cultivation of science, and that we should not waste our resources unnecessarily in other directions. For in arts, literature, philosophy and architecture we can at best imitate our fore-fathers of the early age, but never surpass them in their achievements. This is true not only for India, but for all other civilized nations as well. I might quote in this connection the words of the eminent physicist, Sir Walter Rayleigh who, in course of an address as early as in 1911, spoke as follows :

"The question is not by how much we can excel our fathers, but whether with toil and pains we may make ourselves worthy to be ranked with them. In the beautiful art which models the human figure in stone or some other enduring material, who can hope to match the Greeks? In the art of building who can look at the crowded confusion of any great modern city, with all its fussy and meaningless wealth of decoration, like a pastry cook's nightmare, and not marvel at the simplicity, the gravity, the dignity and fitness of the ancient classic buildings? How can the seasoned wisdom of life be better or more searchingly expressed than in the words of Virgil or Horace, not to speak of more ancient teachers?"

What held good for 1911, holds today with an ever increasing significance. Science should, therefore, be pursued not only for the material benefits and advantages it brings, but also as the only possible avenue open to man through which he can proceed to explore the regions of knowledge still unknown, in search for the ultimate truth or reality which alone can give a meaning to human life. It goes without saying that this is the avowed objective of all learned societies, and we should particularly bear this in mind while celebrating the Silver Jubilee of our Society. At the same time I may be permitted to remind the Government and the public that they owe a great debt to scientific inquirers and scientific workers for the manifold material advantages they enjoy today and hope to enjoy in ever increasing amount in future, and that they should consider it as a sacred duty to promote by all means the development of scientific training and scientific research in the country. For, constant blessings of science like constant pressure are apt to remain unrecognized. Let me stress this once again in the words of Sir Walter Rayleigh, from the address already referred to, where he says :

"It is so easy to use the resources of civilization that we fall into the habit of regarding them as if they were ours by right. They are not ours by right; they come to us by free gift from the thinkers."

I would now like to discuss here one of the burning problems of the day, with which we as scientists are vitally concerned. I mean the problem of the medium of instructions and expression for science in free India today. In my address at the last Annual General Meeting of the Society at Patna I dwelt on this question at some length, and I need offer no apology for reverting to it again on this occasion in view of its paramount importance to the pursuit and growth of science in India, and in view of the fact that there is a state of indecision nay, if I may be permitted to say, a chaotic confusion about it in the minds of many including the scientists themselves. It is obvious that there are two main aspects of the problem which we need consider in a dispassionate manner.

In the first place, it goes without saying that training and instructions, in order to be easily grasped and readily effective, should be imparted in the mother tongue of the trainees, not to speak of the enormous waste of time and energy involved otherwise in learning a foreign language. On the other hand, we should bear in mind that science is international in character and has developed through the co-operative efforts of all the workers of all the lands through all the ages. This co-operation occurs in the form of mental contacts and exchange of ideas, made possible through the publication of scientific

literatures and journals. But the difference of languages stands in the way of an uninterrupted and easy co-operation. So, these two aspects of the problem, relating to the growth of scientific knowledge, seem to conflict somewhat with each other. In Europe and America they have reduced this conflict to a certain extent through the adoption of more or less common scientific terms, symbols and nomenclature. Besides, the three main European languages, viz., English, German and French, in which most of the scientific results of the world are published, are intelligible to practically all prominent scientific workers, who take a good care to have at least a working knowledge of the two more languages other than his own. Let us now consider the conditions under which science has been cultivated in India. Little less than a century ago teaching of science was introduced in Indian colleges through the medium of English language. It might be said that the use of English was an imposition for the purpose; but there was no other alternative, not only for the lack of scientific vocabularies and terminologies, but also for the simple reason of having no common language for India. As a result, the knowledge of science has remained till now confined to only a very small fraction of the educated class, who have had the privilege of scientific studies in the colleges and universities. Science has not been able to reach the mass-mind of the country. But, on the other hand, teaching of science through the medium of English has led to the great advantage of allowing it to be developed on an all-India basis, but for which there would have been possibly no Indian Chemical Society today, nor even the Indian Science Congress Association or the National Institute of Sciences of India. The leaders of Indian thought did not fail to appreciate the beneficial influence of English education in bringing about a political and cultural unity among the enlightened sections of the various linguistic groups, composing the vast population of this sub-continent; and, in fact, they often played the part of pioneers and advocates for the spread of English education in the country. This contact with the western ideas and thoughts undoubtedly exercised a liberalizing influence on the naturally conservative Indian mind; and so far as science is concerned, it has produced in India within the last five or six decades some eminent investigators who have made outstanding contributions in their respective field of study, and have received their due recognition in the world of science.

Let us now examine the probable effects on our scientific activities and studies, that might follow from the replacement of English by an Indian Language as a medium of instruction. To begin with, we must not lose sight of the patent fact that till now India has got no common or national language of its own. Hindi or Hindusthani with *nagri* script has been suggested as the national *lingua franca* for the Indian Union. If science is to be taught and studied in a new or a national language, then we shall have first to coin scientific terminologies and symbols in that language. This is to be followed by the publication of text-books of various standards in different branches of science in the same language. It will evidently involve a prodigious amount of labour extending possibly over 8-10 years for a competent body of scientific and philological experts. Besides, we shall have to train a large body of teachers in this new system for every province. Let us consider in a dispassionate manner how far it will help us in achieving our objective—the rapid development of science in India, on which depends the rapid industrialization of the country, leading to a higher standard of life.



for the common man. Under this new system the study of national language will have to be made compulsory for all the provinces in their schools, colleges and universities; but in many of the non-Hindi speaking provinces, particularly of South India, Hindi is considered to be as much alien a subject as English. So, for these latter at least, substitution of Hindi for English as a medium of instruction will not even eliminate the wastage of time and energy involved in learning a foreign language. Then again, it is not likely to help us in popularizing the ideas and achievements of science among the masses. Because, for the majority of the population in non-Hindi speaking provinces, the national language will, for all intents and purposes, remain as strange as English today. They will not care to learn any new language other than their provincial one, as they will have little occasion to make use of that. Under these circumstances, it appears that the replacement of English by Hindi or Hindusthani for study of science will not lead to any real advantage, but, on the other hand, it is likely to produce a serious retardation to our progress. Then again, English has to be retained in any case as a compulsory second language in our schools, colleges and universities, if we do not want to isolate ourselves from the knowledge of scientific progress of the world. We shall have to depend on English in order to consult the scientific literatures and journals; we shall have to publish the organs of our learned societies in English, if we want to maintain an exchange relation with similar societies of Europe and America undisturbed, and if we desire that our publications should receive due notice in the Scientific Abstracts. In fact, one of the most essential means of acquiring scientific knowledge, namely the exchange of ideas and contact of minds, will cease to exist for us, if English be banished from our courses of study. These are certainly weighty considerations which cannot be altogether ignored, if we do not intend to permit our national welfare and national progress to be arrested by prejudices and prejudices.

As I have said above, India has already acquired an international reputation in the scientific world and she can ill afford to make any rash experiment with her system of education, which may retard the activities of her scientific workers. Our present system of scientific education has been in vogue for near about three quarters of a century. Any radical change or transformation in it cannot be effected without arresting its progress for a while. I cannot express it better than in the inimitable manner of our revered Governor General, who is considered as the wisest man in India today. His Excellency, in course of an address to the staff and students of an educational institution some months ago, was reported to have observed somewhat like as follows :

“ Parts of a machinery cannot be altered if it is to be kept in a running condition. You cannot, in fact, make any major alteration in a railway engine when it is running. If you want to do that, you shall have to stop it altogether.” Any further comment becomes superfluous.

It will, therefore, certainly be of advantage to us to retain the international scientific terminologies and nomenclature unchanged and to continue to use English as the medium for the publication of scientific researches, as well as for discussion in all-India scientific bodies. For scientific instructions in schools and colleges provincial languages

might be liberally introduced for the purpose of explanation and expression during the lecture and class works; this might be substituted by the national *lingua franca* in the Post-Graduate Departments of the Universities, so as to meet the requirements of students from different provinces. In any case, there should be a freedom of choice of language for the teacher, and compulsion should never be allowed to impair the efficiency of teaching. It may also be noted here in passing that well over half of the scientific publications of the world today appear in English, and there is a growing tendency on the part of the many European countries to publish their scientific results in English.

Finally, I might be permitted to refer here to an unwholesome tendency, that seems to have been developing among the Indian Chemists, of segregating themselves into independent groups like the Institution of Chemists, Society of Biological Chemists, Society of Pharmaceutical Chemistry, etc. The last named body, it is reported, has recently duplicated itself into two new autonomous groups under the same name. This fissiparous mentality at the present state of development of chemistry in India cannot be conducive to its progress and healthy growth; for, our resources, both in material and personnel, are rather strictly limited, and we can ill afford to fritter them away in this manner. I take this opportunity of appealing to the organisers of these bodies to consider seriously whether it will not be of real advantage and helpful to them to forge some organic link with the parent body of the Indian Chemical Society.

Though the Indian Chemical Society has not been able to attain the high standard, that we all hoped for at the time of its foundation, nevertheless, the very fact that we are celebrating our Silver Jubilee today after passing through the critical period of an all devastating war and its aftermath, is an evidence of its inner vitality, which will make us recognize in scanty results a call to stronger efforts and urge us on to toil in faith for the fulfilment of our great objective, namely the advancement of knowledge. For, as our sages of the past have said, it is in knowledge that salvation lies.

“ज्ञानम् सत्त्वा परां शान्तिं अचिरमाधिगच्छति ।”

“Jnanam labdha paraam santim achiranadhigachhati.”

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## DISTRIBUTION OF MOLECULAR WEIGHT IN BAMBOO CELLULOSES

BY JAGDISH C. AGGARWALA AND JOSEPH L. MCCARTHY

The celluloses of bamboo wood (*Dendrocalamus strictus*) and also three previously isolated bamboo celluloses have been nitrated, then fractionated by solution or precipitation methods. The degrees of polymerization of the fractions have been estimated by a viscometric method.

The average degrees of polymerization of the cellulose of the bamboo wood, and of the three isolated celluloses, were determined to be about 1620, 1350, 775 and 1260 respectively.

The distribution in molecular weight of the cellulose in bamboo wood, a monocotyledonous angiosperm, is found to be somewhat different from that reported in the literature for the cellulose in the gymnosperms, hemlock and spruce. Celluloses isolated from mixed species of bamboo woods show complex molecular weight distribution curves.

Although there is available considerable chemical and physical evidence (Kita and Azami, *Cellulose Ind. Tokyo*, 1925, **1**, 162; Oguri, *ibid.*, 1933, **9**, 59; *J. Soc. Chem. Ind. Japan*, Suppl. binding, 1932, **35**, 400), that the cellulose of bamboo wood is essentially similar in structure to that of cotton, no study of distribution of molecular weight of bamboo cellulose seems to have been carried out in spite of the both theoretical and practical importance (Spurlin, 'Cellulose and Cellulose Derivatives', edited by Emil Ott, Interscience Publishers, Inc., New York, N. Y., 1946, pp. 930—942) of this characteristic. Thus, in the present investigations the recently reported technique of Mitchell (*Ind. Eng. Chem.*, 1946, **38**, 843) has been employed with bamboo wood to determine the molecular weight distribution of its carbohydrates. Three isolated bamboo celluloses, separated from wood by various procedures, have also been studied.

### EXPERIMENTAL

*Materials.*—The internode portion of an old (about ten years) culm of bamboo wood (*Dendrocalamus strictus*), nearly 25 inches in girth, was reduced to fine shavings. Three unbleached bamboo celluloses were kindly supplied to the authors from sources in India. Cellulose A (from the Forest Research Institute, Dehra Dun, U. P.) was prepared from bamboo (*Dendrocalamus strictus*) by a well-controlled 'fractional digestion' procedure (Bhargava, Indian Forest Bulletin, 1945, No. 129) using as reagents a mixture of sodium hydroxide and sodium sulphide. Cellulose B (from Bengal Paper Mills Ltd., Raniganj, Bengal) was secured from mixed species of Indian bamboos, also by a fractional digestion treatment with an alkaline aqueous solution. Cellulose C (from India Paper Pulp Company Ltd., Naihati, Bengal) was isolated from

mixed species of Indian bamboos by acidic digestion with a 4.5% solution of magnesium bisulphite.

*Nitration.*—Both the bamboo wood and the celluloses were nitrated using a mixture consisting of  $\text{HNO}_3$  (64% by weight),  $\text{H}_3\text{PO}_4$  (26%) and  $\text{P}_2\text{O}_5$  (10%). The methods of nitration, of stabilization, and of washing the nitrocelluloses free from nitrolignins and other non-cellulosic impurities were essentially those described by Mitchell (*loc. cit.*). Weight yields of nitrate from celluloses A, B and C were 159, 157 and 155% respectively.

*Fractionation of Cellulose Nitrate.*—The cellulose nitrates obtained from bamboo wood and from celluloses A and C were divided into fractions having different molecular weights by a fractional precipitation method in a water-acetone system as suggested by Zurisch (*Chem. Ztg.*, 1940, 64, 269). The nitrate of cellulose B yielded eleven fractions by a fractional solution method (Mitchell, *loc. cit.*) using appropriate solvent mixtures of ethanol (95%) and ethyl acetate.

*Viscosity of Cellulose Nitrate Solutions.*—Solutions of the cellulose nitrates were prepared at concentrations of 0.5 g. of nitrate per liter of C. P. ethyl acetate or C. P. acetone. The viscosity of these solutions was determined, usually at  $20.5 \pm 0.1^\circ$ , using Cannon-Fenske type viscometers (*Ind. Eng. Chem. Anal. Ed.*, 1938, 10, 297). Since the viscosity of the dilute cellulose nitrate solutions tended to decrease on standing, a solution was rapidly effected and viscosities were measured without delay.

*Calculation of Degree of Polymerization.*—From the times of outflow from the viscometer for the pure solvent ( $t_0$ ), and each cellulose nitrate solution ( $t$ ), the relative viscosity ( $\eta_r$ ), the specific viscosity ( $\eta_{sp}$ ), the intrinsic viscosity  $[\eta]$ , and finally the degree of polymerization (D. P.) were calculated by use of the following relationships:

$$\eta_{sp} = \eta_r - 1 = \frac{t}{t_0} - 1 \quad \dots \quad (1)$$

$$[\eta] = \frac{\eta_{sp}}{c} = \frac{1}{K} \quad \dots \quad (2)$$

$$\text{D. P.} = K [\eta] \quad \dots \quad (3)$$

where the concentration of nitrocellulose ( $c$ ) is in g./100 c. c. of solvent.

The value of the constant " $K$ " was determined graphically for a particular cellulose nitrate-solvent system by plotting  $(\eta_{sp}/c)$  against  $(\eta_{sp})$  for different concentrations as suggested by Huggins (*Ind. Eng. Chem.*, 1943, 35, 982). These plots were found to be linear. The ratio of the slope to intercept in these plots, at the point of zero concentration, gave the value of " $K$ ". It was found to vary from 0.312 to 0.350 for cellulose nitrate in ethyl acetate, depending upon

temperature and the extent and nature of impurities associated with the polymer. The constant  $K$  was taken as 100 (cf. Mitchell, *loc. cit.*).

An average degree of polymerization was calculated for the unfractionated celluloses from data secured from the several fractions by use of the relationship

$$\text{D. P. (Ave.)} = \frac{\sum(w)}{\sum(w)} (\text{D. P.})$$

where  $w$  is the weight of a particular fraction and "D. P." is its degree of polymerization.

TABLE I

*Study of nitration of bamboo cellulose B.*

Expt. No.	Amount of cellulose.	Time of nitration.	Percentage*† yield.	$\eta_{sp}$ ‡	Average D. P.
I	1.375 g.	20 hrs.	143.5	0.182	818
II	1.375	6	150.2	0.500	815
III	1.375	4	151.0	0.530	882
IV	8.750	6	157.2	0.517	877
V	8.750	2	155.0	0.183	820
VI	8.750	0.5	157.1	0.521	875

\* In all cases nitration was conducted at  $20 \pm 0.5^\circ$  using 350. g. of the nitrating acids.

† Calculated on air-dry basis. The nitrates from all experiments were completely soluble in ethyl acetate.

‡ Efflux time with C. P. ethyl acetate at  $25^\circ = 2.30$  min,  $\eta_{sp}$  is for 0.05% solution in ethyl acetate at  $25^\circ$ .

§ Taking  $K=100$  and  $K'=0.35$ .

TABLE II

*Fractionation of nitrocellulose\* from bamboo wood.*

Fraction number.	Cumulative amount of water added.	Wt. of fraction	Cumulative wt. pptd.	*Efflux time for viscosity.	† D. P.
I	51.0 c.c.	0.2103 g.	15.92 %	6.75 min	2328
II	63.0	0.1110	26.73	5.92	2030
III	78.0	0.1895	41.01	5.34	1805
IV	100.0	0.2781	62.06	5.05	1680
V	125.0	0.1512	73.48	4.78	1550
VI	150.0	0.1250	82.89	4.25	1285
VII	175.0	0.0380	85.78	3.70	975
VIII	200.0	0.0758	91.50	3.28	710
IX‡	Not. pptd.	0.1124	100.00	2.95	482

Total 1.3243

\* Total amount of material used for fractionation by precipitation at  $21^\circ$  was 1.3281g. in 425 c.c. solution.

\*\* Efflux time is for 0.05% solution in C. P. ethyl acetate at  $20.50^\circ$ . Efflux time for C. P. ethyl acetate itself was 2.34 min.

† D. P. was calculated using value of  $K'=0.33$  and  $K=100$ .

‡ Last fraction obtained by evaporation of the solution to dryness on a water-bath.

TABLE III

*Fractionation of nitrocellulose\* from bamboo cellulose A.*

Fraction number.	Cumulative amount of water added.	Wt. of fraction.	Cumulative wt. pptd.	**Efflux time for viscosity.	†D. P.
I	35.0 c.c.	0.0826 g.	5.80%	6.62 min.	2205
II	37.0	0.1281	11.80	6.31	2100
III	42.0	0.2310	31.25	5.74	1892
IV	49.0	0.2965	52.07	5.17	1655
V	53.0	0.1592	63.24	4.65	1416
VI	62.0	0.1515	73.87	4.27	1220
VII	72.0	0.0576	77.91	3.54	802
VIII	82.0	0.0399	80.71	3.28	635
IX	95.0	0.0462	83.96	3.05	479
X	115.0	0.0986	90.88	2.88	358
XI‡	Not pptd.	0.1310	100.00	2.50	165

Total 1.4252

\* Total amount of material used for fractionation by precipitation at 22° = 1.4266 g. in 320 c.c. solution.

\*\* Efflux time is for 0.05% solutions in C. P. ethyl acetate at 20.5°, efflux time for C. P. ethyl acetate itself was 2.42 min.

† D. P. was calculated on the basis of  $K=100$  and  $K'=0.33$ .

‡ Last fraction obtained by evaporation of solution to dryness on a water-bath

TABLE IV

*Fractionation of nitrocellulose\* from bamboo cellulose B.*

Fraction number	Solvent mixture composition* **		Weight of fraction.	Cumulated wt. dissolved.	†† Efflux time.	‡ D. P.
	Ethyl alcohol†	Ethyl acetate.				
I	100.00	0.0	0.1600 g.	1.55%	2.35 min.	22
II	70.00	30.0	0.1490	2.99	2.35	43
III	60.00	40.0	0.0535	3.39	2.56	217
IV	50.00	50.0	0.3815	7.12	3.12	632
V	45.00	55.0	1.2885	19.57	3.21	697
VI	42.00	58.0	1.7521	36.57	3.25	722
VII	40.00	60.0	1.1169	47.84	3.27	735
VIII	37.00	63.0	1.6350	63.44	3.40	820
IX	35.00	65.0	1.7003	79.86	3.48	870
X	32.00	68.0	1.4932	94.31	3.58	930
XI	30.00	70.0	0.5613	100.00	3.64	966

\* Total amount of material used for fractionation by solution method at 25° = 10.0 g.

\*\* Composition is by volume.

† 95% ethyl alcohol was used.

†† Efflux time is for 0.05% solution in C. P. ethyl acetate at 25° except for fraction I, for which it is for 0.1% solution.

‡ D. P. was calculated using  $K'=0.35$  and  $K=100$ .

TABLE V

*Fractionation of nitrocellulose\* from bamboo cellulose C.*

Fraction number.	Cumulative amount of water added.	Weight of fraction.	Cumulative wt. pptd.	**Efflux time for viscosity.	†D. P.
I	38.0 c. c.	0.2036 g.	14.85%	3.66 min.	1890
II	39.0	0.0680	19.73	3.52	1795
III	41.0	0.0975	26.73	3.39	1705
IV	43.0	0.1605	38.38	3.14	1512
V	46.0	0.1237	47.26	3.00	1390
VI	49.0	0.1431	57.56	2.89	1285
VII	54.0	0.1112	65.77	2.85	1245
VIII	60.0	0.1510	79.09	2.82	1215
IX	70.0	0.1055	86.64	2.31	587
X	100.0	0.0530	90.48	2.20	416
XI‡	Not pptd.	0.1323	100.00	2.08	110
		1.3924			

\*Total amount of material used for fractionation by precipitation at 22°=1.3720 g in 320 c. c. of solution.

\*\*Efflux time is for 0.05% solution in C. P. acetone at 20.5°. Efflux time for C. P. acetone at 20.5° was 1.97 min.

†D. P. was calculated on basis of  $K=100$  and  $K'=0.168$ .

‡Last fraction obtained by evaporation of the solution to dryness on a water bath.

## DISCUSSION

Since Berl and Rueff (*Cellulosechem.*, 1931, 12, 53; 1933, 14, 115) showed that cellulose could be nitrated and renitrated without appreciable depolymerization by use of a nitrating mixture containing phosphoric acid and phosphorous pentoxide but no sulphuric acid, a readily carried out method has been at hand whereby cellulose can be converted into a soluble nitrate amenable to molecular weight distribution studies by use of well-known techniques for fractionation and for molecular weight determination.

To secure undegraded and yet completely soluble cellulose nitrates, however, the nitrating reaction must be properly conducted. Thus, in the present investigation, cellulose B was nitrated under a number of reaction conditions and for each cellulose nitrate prepared its weight-yield, solubility in ethyl acetate, and its average degree of polymerization were determined (Table I). Since all nitrates were entirely soluble in ethyl acetate, the reaction conditions giving the highest degree of polymerization (*i. e.* Expt. VI) were those chosen and used in subsequent work with the isolated bamboo celluloses. Bamboo wood was nitrated using Mitchell's conditions (*loc. cit.*).

The weight-yield of cellulose nitrate obtained from bamboo wood was 91.2%, calculated on an extractive-free basis. With hemlock wood Mitchell (*loc. cit.*) obtained a yield of 120–130% under identical conditions, while for pure cellulose the yield should be 180%. Extractive-free bamboo wood

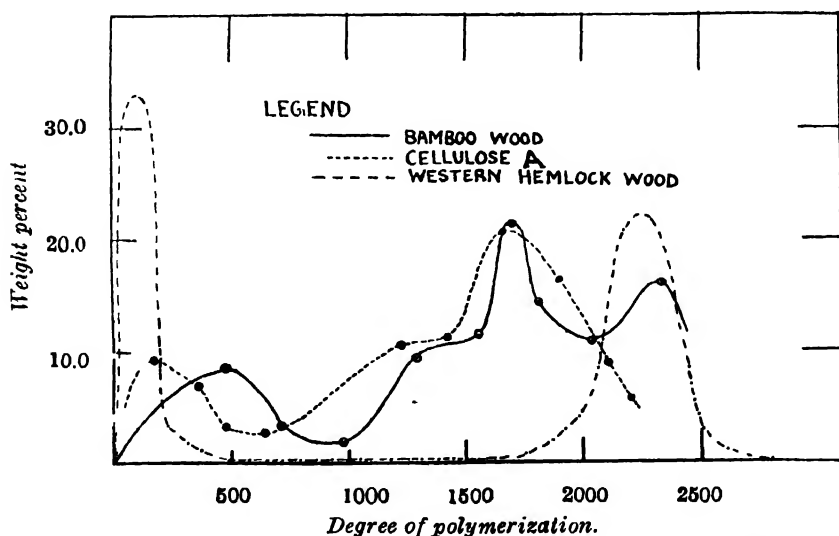
(*Dendrocalamus strictus*) has been reported to contain on the average 64% of Cross and Bevan cellulose (cf. Bhargava, *loc. cit.*). Had all this cellulose in the bamboo wood been recovered as cellulose nitrate, the weight-yield expected is about 115%. The deviation of the actual yield from this theoretical value suggests that some of the carbohydrates in bamboo wood, which are isolated as Cross and Bevan cellulose, differ in characteristics from those in hemlock. The yields secured on nitration of the isolated bamboo celluloses were also found to be less than those anticipated from theory.

The nitrates obtained from bamboo wood, and from celluloses A and C were fractionated by the precipitation procedure of Zurisch (*loc. cit.*), in preference to the solution method of Mitchell (*loc. cit.*) used earlier with the nitrate of cellulose B, because the latter technique was time consuming and since gelatinization occurred which gave rise to difficulty in separating liquid and solid phases. With Zurisch's method, the extent of precipitation at a particular state of the system was found to be quite reproducible. The average degree of polymerization of the celluloses in several fractions was estimated by viscometric procedures.

By integration of the fractionation data (Table II), the average degree of polymerization of the celluloses from bamboo wood was calculated to be about 1620, which corresponds to a molecular weight of about 260,000. This is considerably less than Mitchell's (*loc. cit.*) average value of 2000 found for the carbohydrates of Western hemlock wood (*Tsuga heterophylla*), but higher than that of Atchison (*Paper Trade J.*, 1943, 116, No. 22, 23-34) of 1450 for holocellulose from spruce wood (*Picea mariana*).

However, with respect to distribution of molecular weights (Fig. 1), the celluloses of hemlock (Mitchel, *loc. cit.*) and spruce (Atchison, *loc. cit.*)

FIG. 1



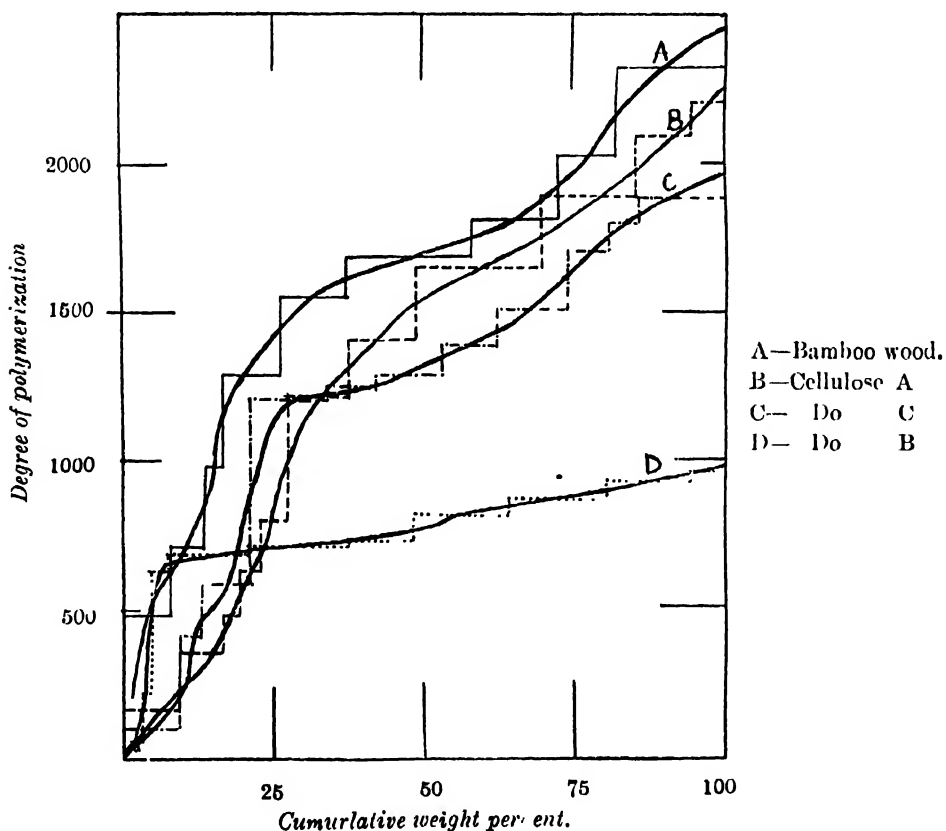
woods are about entirely either of rather high (more than 2000) or else quite low (less than 500) degree of polymerization, with intermediate celluloses being



present only in small proportion. On the other hand, nearly 65% of the cellulose from the bamboo wood are found to be of intermediate degree of polymerization (500 to 2000), with only about 10 and 26% being of lower and higher, respectively. Two maxima in frequency of distribution are observed in the higher range. Molecular weight distribution difference between the carbohydrates or cellulose of bamboo and those of hemlock and spruce may arise because of differences in botanical characteristics of hemlock and spruce as gymnosperms, compared to bamboo as a monocotyledonal angiosperm.

Isolation of cellulose from woods by use of aqueous solutions of alkaline or acidic reagents to accomplish delignification usually is accompanied by the dissolving into the aqueous reagent solutions of some low molecular weight carbohydrates; thereby the average molecular weight of the remaining isolated cellulose tends to be higher than that of the total carbohydrates originally present in the wood. This isolation procedure simultaneously tends to depolymerize the carbohydrates and may alter them in other ways. Both tendencies will be reflected in the distribution of molecular weights in isolated celluloses. Fractionation data for cellulose A is given in Table III. The differential

FIG. 2



distribution curve found for bamboo wood carbohydrates compared with that for cellulose A (Fig. 1), both from *Dendrocalamus strictus*, shows a general

shifting of the curve to somewhat lower levels in degree of polymerization as might be expected from hydrolytic influences acting during the isolation reaction. This trend is affirmed by the average degree of polymerization of about 1350 found for isolated cellulose A compared with that of about 1620 found for the cellulose of bamboo wood. Bamboo cellulose B appears to have been markedly reduced in average molecular weight in the course of its isolation from mixed species of bamboos under alkaline conditions (D. P. = 775), while the acidic conditions of delignifications used to secure Cellulose C did not yield serious decrease in degree of polymerization (D. P. = 1260). The complex trends in the integral molecular weight distribution curves for cellulose B and C (Fig. 2) are probably to be traced to the fact that mixed species of bamboo wood were used for preparation of these celluloses.

The authors gratefully acknowledge the aid of the Bengal Paper Mill Ltd., Raniganj; the India Paper Pulp Company Ltd., Naihati; and the Forest Research Institute, Dehra Dun, India, for supplying materials. They also wish to express their appreciation to the Ministry of Education of the Government of India for grant of an Overseas Stipend to one of us (J. C. A.).

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## PRODUCTION OF JOSHI EFFECT IN SULPHUR DIOXIDE UNDER SILENT ELECTRIC DISCHARGE

BY G. S. DESHMUKH AND U. S. DHAR

Under ozoniser discharge  $\text{SO}_2$  shows a marked *negative Joshi effect* (33% at maximum). At constant applied kV, it decreases with pressure  $p$  beyond a certain limit. At constant  $p$  increase of kV decreases it. *Positive Joshi effect*  $+\Delta i$ , is observed at low kV. It decreases precipitously by a small increase in kV; further increase first abolishes it and then inverts it to  $-\Delta i$ . 'Ageing' under discharge diminishes the effect markedly due to  $\text{SO}_2$  condensation from  $\text{SO}_2$  decomposition, since a pre-formed  $\text{SO}_3$  film inhibits  $-\Delta i$  in  $\text{SO}_2$ , that of NaOH enhances it. Results support Joshi's theory of the surface origin of the phenomenon.

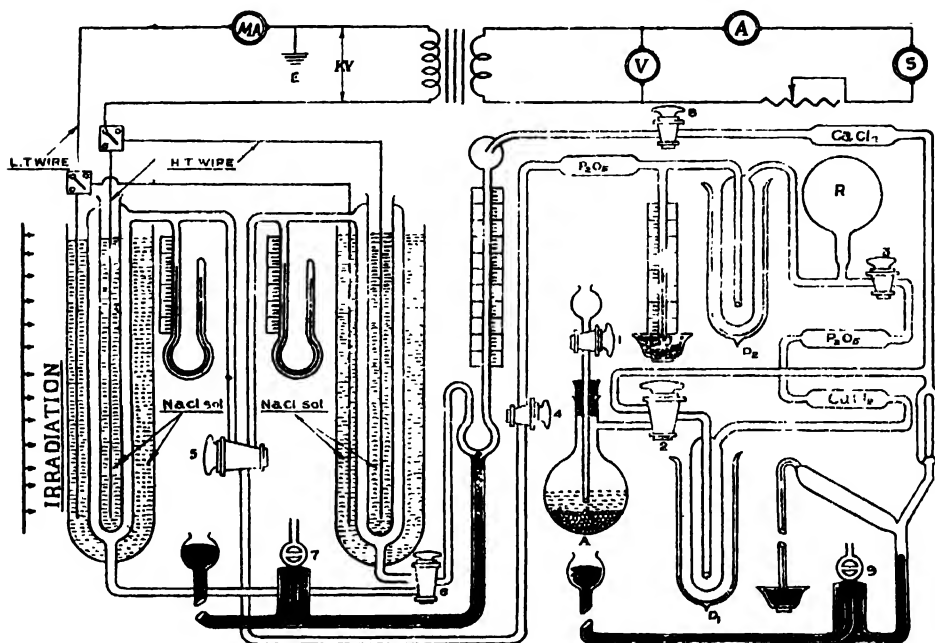
Soon after the discovery of the negative Joshi effect  $-\Delta i$  (Joshi, *Proc. Indian Sci. Cong.*, 1943, Part II, pp. 70-75), an instantaneous and reversible photodiminution of the current  $i$  in a number of elementary gases, the positive Joshi effect,  $+\Delta i$ , was observed in iodine vapour in the presence of a surface film of KI and  $\text{KI}_3$  (Joshi and Murthy, *Proc. Indian Sci. Cong.*, 1942, Part III, p. 64), in nitrogen peroxide (Joshi and Visvanathan, *ibid.*, p. 66), oxygen (Joshi and Cherian, *ibid.*, p. 58) and bromine (Deshmukh and Sirsikar, *J. Amer. Chem. Soc.*, communicated). The presence of impurities and 'wall effect' in electrically excited system had a marked influence on the production of the Joshi effect (Shukla, *Proc. Indian Sci. Cong.*, 1948, Part III, *Chem. Sec.*, p. 12). Sulphur dioxide gas under silent electric discharge was found to produce as decomposition products, annular films of sulphur trioxide and sulphur, in addition to the undecomposed gas, oxygen and two other unidentified solids (Joshi and Sharma, *J. chem. phys.*, 1943, 31, 511). It was of interest therefore to extend the observations of the phenomenon to sulphur dioxide gas and to investigate the rôle of its products of decomposition on the production of the Joshi effect.

### EXPERIMENTAL

The general arrangement of the apparatus and the electrical circuit employed are shown in Fig. 1. Sulphur dioxide gas was prepared by the action of concentrated sulphuric acid on sodium bisulphite in A. The gas was led slowly through a series of tubes charged with  $\text{P}_2\text{O}_5$  and  $\text{CaCl}_2$ , and stocked in the reservoir R. It was next purified by freezing it in the traps  $\text{D}_1$  and  $\text{D}_2$ , cooled by liquid air. The uncondensable portion was removed with the töpler. The

condensed  $\text{SO}_2$  in  $\text{D}_2$  was then allowed to evaporate. The first and the last fractions of the gas were rejected ; the middle fraction was stored in R.

FIG. 1



The discharge was produced in the annular space of a Siemens' type (glass) ozoniser ; two such ozonisers were used (see Fig. 1). The ozoniser was connected through the drying tubes to the reservoir R by proper manipulation of the taps  $T_4$  and  $T_5$ , and directly to the mercury manometer and the töpler through the tap  $T_6$ . A given series of experiments was commenced only after the entire assembly had maintained a satisfactory vacuum for at least 48 hours.

The ozoniser was excited by a transformer discharge of 50 cycles frequency in the primary supply. The primary potential  $V$  (except when too low) was recorded with an A. C. voltmeter ; the secondary potential in kilo-volts (r. m. s.)  $kV$ , was calculated from a knowledge of  $V$  and the step-up ratio of the transformer, viz., 267. The system was irradiated transversely to the ozoniser axis, by operating a shutter between it and two 100 watts incandescent (glass) bulbs run at 220 volts. The inner electrode of the ozoniser was connected to the transformer secondary ; the other was earthed. The discharged current,  $i$ , was measured with a milliammeter or a reflection type galvanometer actuated by a metal-oxide rectifier, introduced in the low tension line of the ozoniser circuit. From observations of the current  $i_D$ , when the ozoniser was screened from the light, and when exposed to it  $i_L$ , the net joshi effect,  $\Delta i$ , is given by  $i_D - i_L$  ; its relative value  $\% \Delta i$  is  $100 \Delta i / i_D$ .

As found by Joshi and Sharma (*loc. cit.*) the dielectric strength of  $\text{SO}_2$  was high. Decompositions were produced therefore at moderate gas pressures within the range of 9 to 180 mm. up to 8 kV applied to the ozoniser. The general progress of the decomposition, as followed by the pressure-time observations, showed a progressive but small fall of pressure during the initial and limited period of exposure to the discharge. Further continuation of the discharge resulted in a state during which the pressure decreased extremely slowly. In agreement with the results of Joshi and Sharma (*loc. cit.*) the decomposition under silent discharge of  $\text{SO}_2$  gave  $\text{SO}_3$ , free sulphur, oxygen and traces of two solid products (not identified).

The procedure in respect of observations of the Joshi effect in  $\text{SO}_2$ , as indicated by the general results mentioned above, was as follows: The purified gas was admitted into the annular space of the ozoniser at a low pressure. The values of  $i_0$  and  $i_1$  were then noted at a series of increasing applied potential kV. This was changed to the next higher value only when the rate of decomposition became negligibly small as judged by the (sensible) constancy of the pressure of the decomposition mixture. Thus *e.g.*, during the first series of results under Table I, the extent of decomposition of  $\text{SO}_2$  corresponded to a pressure change of only 1.5 mm. *i.e.* about 6.2%. The contents of the annular space were tóplered out and a fresh sample of the purified gas (from the same stock as before) was introduced at a pressure slightly higher than the previous value. Results for  $i_0$ ,  $i_1$ ,  $\Delta i$  and  $\% \Delta i$  were recorded once more (at  $p=30$  mm.), until, as in the previous series, a state of practically arrested decomposition ensued; the final pressure diminution now produced was 6 mm. *i.e.* 20% of the initial pressure. After this, once again the gaseous products were tóplered out, fresh  $\text{SO}_2$  introduced at a higher pressure, and so on, in successive series. Table I contains data of one of a number of groups of such results obtained. For want of an A. C. voltmeter during this stage of work, results are given for the total ozoniser current in milli-amps, mA. These values served as an index of the corresponding variation of the actual potential applied to the ozoniser.

The series of data in Table II were obtained in a way similar to that followed in Table I. The ozoniser now used was different from that in Table I; its electrodes were fitted with a ground joint, instead of a sealed one (as in Table I). In this series the pressure of  $\text{SO}_2$  was increased progressively over the range of 9 to 47 mm., the exciting potential being varied from 1.8 to 8 kV. Table II is typical of a series of results in which the *positive* Joshi effect (*i.e.* a photo-increase of the current  $i$ ) was observed at low exciting kV.

For reasons explained later, it was of interest to investigate the production of Joshi effect in  $\text{SO}_2$  in presence of certain annular films, *viz.*, sodium sulphate, sodium hydroxide and mercuric chloride. For this part of the work a new ozoniser (*vide infra*), also fitted with a ground joint, was employed. The inside surface of the outer tube and the outer surface of the inner tube were

smearcd carefully with concentrated aqueous solution of each of the above substances. The electrodes were then fitted together and the entire system exhausted *slowly* but completely over the töpler. Purified  $\text{SO}_2$  was then admitted in successive samples at increasing pressures and  $i_D$ ,  $i_L$ ,  $\Delta i$  and  $\% \Delta i$  were observed with each electrode film as described in Table II. These results for the three films mentioned above, in contact with  $\text{SO}_2$  in the pressure range of 16 to 60 mm. and excited under the discharge at 1 to 6 kV, are recorded in Table III.

TABLE I  
Ozoniser A

Initial pressure $p$ of $\text{SO}_2 = 24$ mm. Diminution in $p = 1.5$ mm., 6.2%.				
$i$ (in mA).	$i_D$ .	$i_L$ .	$\Delta i$ .	$\% \Delta i$ .
0.04	8.4	6.4	-2.0	-24
0.06	15.6	13.6	-2.0	-13
0.10	35.6	32.6	-3.0	-8.4
0.16	62.0	58.6	-3.4	-5.4
0.20	82.0	76.0	-6.0	-7
0.24	99.4	95.1	-4.0	-4
0.26	109.4	104.1	-5.0	-4.5
0.30*	129.0	125.0	-4.0	-3
Initial $p$ of $\text{SO}_2 = 30$ mm. Diminution in $p = 6$ mm., 20%.				
0.10	15	10	-0.5	-33
0.20	12.0	10.0	-2.0	-7
0.26	14.0	12.0	-2.0	-14
0.30	27.0	23.5	-3.5	-13
0.34*	32.5	30.0	-2.5	-8
Initial $p = 55$ mm. Diminution in $p = 8$ mm., 15%				
0.04	7.2	6.6	-0.6	-8
0.06	15.0	14.4	-0.6	-3.5
0.08	23.0	22.2	-0.8	-3
0.10	34.0	33.4	-0.6	-2
0.14	53.4	53.0	-0.4	-1
0.16	62.0	61.8	-0.2	-0.3
0.18	71.2	71.0	-0.2	-0.3
0.20	79.8	79.6	-0.2	-0.25
0.24*	105.4	105.4	...	...

\* Decomposition products were töplered out at this stage and fresh  $\text{SO}_2$  from the same stock was introduced.

TABLE II

## Ozoniser B

Initial  $p$  of  $\text{SO}_2$  = 9 mm. Diminution in  $p$  = 1 mm., 11%.

kV.	$i$ (mA).	$i_D$ .	$i_L$ .	$\Delta i$ .	% $\Delta i$ .
1.8	0.06	21.4	25.0	+3.6	+17
2.3	0.08	28.0	30.0	+2.0	+7
3.2	0.10	37.0	37.0	...	...
4.5	0.12	45.0	41.0	-4.0	-2
5.3	0.14	55.4	54.0	1.4	-2.5
5.9	0.16	67.4	66.0	1.4	2
6.2	0.18	73.0	72.4	-0.6	0.8
6.9	0.20	81.0	83.4	-0.6	-0.7
8.0*	0.21	98.0	98.0	...	...

Initial  $p$  = 18 mm. Diminution in  $p$  = 2 mm., 11%.

1.3	0.04	16.6	18.6	+2.0	+12
2.1	0.06	28.0	31.0	+3.0	+11
2.7	0.08	43.6	47.0	+3.4	+8
4.1	0.10	61.0	61.0	...	...
4.9	0.14	73.6	71.6	-2.0	-3
5.6	0.16	85.6	80.6	-5.0	-6
6.5	0.20	112.0	103.0	-9.0	-8
6.9	0.22	122.0	116.0	-6.0	-5

\* Decomposition products were tumbled out at this stage and fresh  $\text{SO}_2$  from the same stock was introduced.

At successive higher pressures of  $\text{SO}_2$  (*i. e.* 42 mm., 47 mm. etc.) the Joshi effect was not observed.

TABLE III

Ozoniser C (with a coat of  $\text{Na}_2\text{SO}_4$ ).Initial  $p$  of  $\text{SO}_2$  = 16 mm. Diminution in  $p$  = 2 mm., 12.5%.

kV.	$i$ (mA).	$i_D$ .	$i_L$ .	$\Delta i$ .	% $\Delta i$ .
1.7	0.04	22.0	19.4	-2.6	-12
2.5	0.08	38.6	37.8	-0.8	-2
4.2*	0.12	56.4	56.4	...	...

Initial  $p$  of  $\text{SO}_2$  = 31 mm. Diminution in  $p$  = 7 mm., 22.6%

1.6	0.04	11.6	9.6	-2.0	-17
2.8	0.08	36.0	34.6	-1.4	-4
3.9	0.12	56.0	55.0	-1.0	-2
4.8	0.16	82.4	81.4	-1.0	-1
5.6*	0.20	103.0	103.0	...	...

TABLE III (contd.)  
Ozoniser C (with a coat of NaOH)

Initial  $p$  of  $\text{SO}_2 = 26$  mm. Diminution in  $p = 2$  mm, 7.7%

kV.	$i$ (mA)	$i_D$	$i_L$	$\Delta i$	% $\Delta i$
1.3	0.04	20.0	17.0	- 3.0	- 15
2.1	0.08	41.0	35.0	- 6.0	- 14
2.9	0.12	68.0	58.0	- 10.0	- 14
4.0	0.16	90.0	71.0	- 19.0	- 21
5.1*	0.20	111.0	98.0	- 13.0	- 12

\* Decomposition products were topolered out at this stage and fresh  $\text{SO}_2$  from the same stock was introduced.

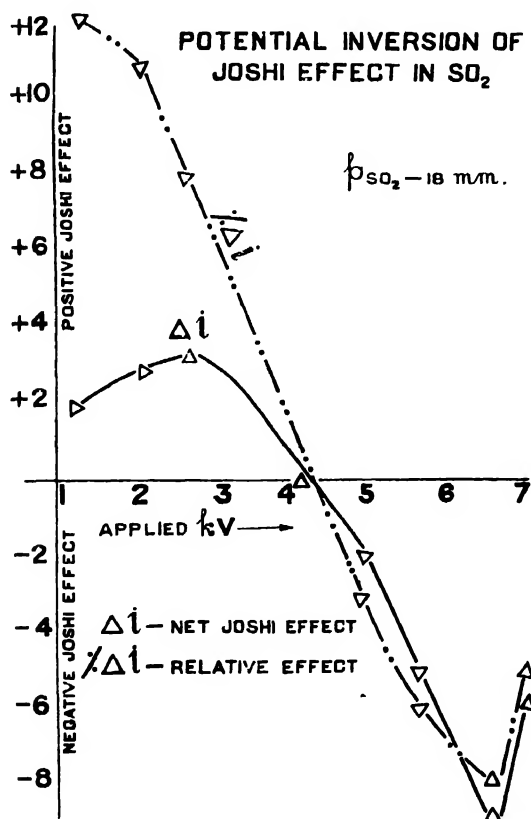
Initial  $p$  of  $\text{SO}_2 = 59$  mm. Diminution in  $p = 9$  mm., 15.2%

2.3	0.04	15.0	14.0	- 1.0	- 7
2.9	0.08	38.0	32.0	- 6.0	- 16
3.7	0.12	66.0	57.0	- 9.0	- 14
4.7	0.16	90.0	79.0	- 11.0	- 12
5.7*	0.20	129.0	123.0	- 6.0	- 5

### DISCUSSION

Tables I to III and Fig. 2 which contain but typical results, show that both the positive and (the more familiar) negative Joshi effect,  $\pm \Delta i$  are

FIG. 2



produced in  $\text{SO}_2$  under electric discharge. It is seen that at a constant applied kV the Joshi effect is first increased and then reduced by increasing the gas



pressure,  $p$ . Thus *e.g.*, at a kV corresponding to 0.1 mA (see Table I) the relative Joshi effect,  $\% \Delta i$ , increases from 8 to 30 as  $p$  is increased from 24 to 30 mm., a further increase of pressure to 55 mm. reduces  $\% \Delta i$  to 2.0. The relative effect was maximum at low exciting potential and decreased by increasing the applied kV. Both these deductions are in agreement with the generality of the findings from these laboratories in regard to  $\Delta i$  phenomenon. The possible influence of the products of decomposition of  $\text{SO}_2$  under the discharge on its characteristic Joshi effect is considered later. It may be recalled that soon after the discovery of the negative Joshi effect, the positive effect,  $+\Delta i$  was observed in iodine vapour excited in the presence of a surface film of  $\text{KI} + \text{KI}_3$  in nitrogen peroxide, oxygen, air and bromine (Joshi and co-workers, *loc. cit.*). Data in Table II extend these observations to  $\text{SO}_2$ . It is remarkable to observe that a positive Joshi effect, as large as 17% photo-increase of current, is produced at 1.8 kV which is the lowest applied potential. As observed in the case of negative Joshi effect, the positive effect diminishes by increasing the applied kV. It is, however, interesting to observe that in the above series (Table II), but a moderate increase in the applied kV causes a precipitous decrease in the Joshi effect to practically zero; and what is significant, reverses its sign so as to give an appreciable  $-\Delta i$  (see Fig. 2), at a large kV. This influence of the applied potential kV on the positive Joshi effect and the reversal of its sign are in complete accord with the results in other system (*loc. cit.*). Unlike single system, such as excited iodine and under certain conditions chlorine, it was not possible to reproduce the positive effect, mentioned above, by decreasing the applied kV to the initial low value. This may be attributed to the non-reversible change in the nature of the system as a result of the chemical decomposition produced under the discharge (Joshi and Sharma, *loc. cit.*).

Whilst due to comparatively high insulating power of  $\text{SO}_2$ , discharge could be produced only at low gas pressure (below 180 mm.) up to 8 kV (largest used), it was observed that the decomposition produced, as judged by reduction of the over-all pressure, was about 10%, during by far the major period of  $\Delta i$  observations. In each of the experiments made, however, it was significant to observe a sharp decrease in the magnitude of the Joshi effect  $\Delta i$  during the initial stage of the discharge. Thus *e.g.*, when  $\text{SO}_2$  was introduced in the fresh ozoniser at 24 mm. (Table I), the gas pressure diminished progressively to 22.5 mm in about 40 minutes of exposure to the discharge. During this period the relative Joshi effect,  $\% \Delta i$ , decreased from an initial 24 to 3, although by far the major part of  $\text{SO}_2$  introduced remained undecomposed, as was observed subsequently by analysis of the decomposition mixture at this stage. This revealed the presence of oxygen and sulphur, both of which show the Joshi effect to an appreciable extent (*loc. cit.*). It is therefore suggested that the marked diminution (numerically) of  $\% \Delta i$ , as observed, may be associated with the formation of  $\text{SO}_3$ , assuming that the corresponding influence of the traces of two other unidentified solid products of decomposition of  $\text{SO}_2$  is negligible.

The above deduction was further tested. A fresh ozoniser was filled with purified oxygen at 99 mm. and subjected to silent discharge until an appreciable reduction of pressure was effected due to ozone formation. A moderate amount of  $\text{SO}_2$ , purified as described already, was admitted into the annular space of the ozoniser and the mixture allowed to stand over 24 hours. The  $\text{SO}_3$  formed by the interaction of  $\text{O}_3$  and  $\text{SO}_2$  condensed on the annular walls. The mixture was then tóplered out. On introducing various samples of pure  $\text{SO}_2$  in this ozoniser, the Joshi effect was not detectable. Presumably, as a result of exposure to discharge under conditions during experiments, of which those in Table II are but a sample, as also the above experiments with  $\text{SO}_3$  films, the ozoniser walls were denatured in some way with the result that the Joshi effect observed in this ozoniser became negligibly small. Even prolonged cleaning by alkali and hot chromic acid solution failed to restore  $\Delta i$  when the ozoniser was charged with fresh  $\text{SO}_2$  under conditions illustrated by results in Tables I and II.

Similar results suggestive of a pronounced wall effect on the production of  $\pm \Delta i$  have been observed in these laboratories (Shukla, *loc. cit.*). A series of experiments was therefore carried out to examine further the inference drawn above regarding the rôle of the wall-condensed  $\text{SO}_3$  in inhibiting the Joshi effect.

In a fresh ozoniser, fitted with ground joint, it is seen that a pre-formed film of  $\text{Na}_2\text{SO}_4$  does not influence markedly the Joshi effect  $\Delta i$ ; this is, however, favoured by a coat of  $\text{NaOH}$  (Table III). What is more, the diminution of the Joshi effect with 'ageing' *i.e.*, a continuous exposure to discharge at a given applied potential(s)  $V$  does not cause a decrease of the corresponding Joshi effect as was observed in absence of an annular film (cf. Tables I and II). This is explicable since the  $\text{SO}_3$  produced from  $\text{SO}_2$  under the discharge, interacts with the surface alkali to form  $\text{Na}_2\text{SO}_4$ . That a film of  $\text{HgCl}_2$  should abolish the Joshi effect may, in part, be explained by the following suggestions due to Prof. Joshi: It is that  $\pm \Delta i$  being fundamentally of surface origin (Joshi, *Curr. Sci.*, 1947, 16, 19) may be poisoned by  $\text{HgS}$  formed by the interaction of sulphur from  $\text{SO}_2$  and  $\text{HgCl}_2$  (Dasgupta, *unpublished data*). Furthermore, the observations on the production of the Joshi effect in hydrogen (Deshmukh, *J. Indian Chem. Soc.*, 1947, 24, 211) have shown that the presence of  $\text{Hg}$  vapour is a pronounced inhibitor in the production of  $\Delta i$ .

Grateful thanks of the authors are due to Professor S. S. Joshi for suggesting the problem and kind guidance.

## STUDIES IN INDIGOID DYES. PART XI. PHENANTHRATHIOPHENE-INDIGOS

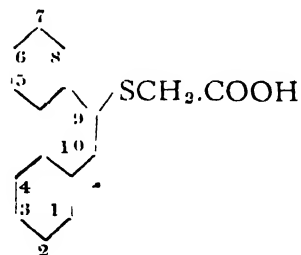
BY PARESH CHANDRA DUTTA

9-Thiolphenanthrene and some of its derivatives have been synthesised by the author with a view to preparing some interesting dyes from the point of view of colour in relation to chemical constitution. Some of these dyes have already been described in part X of this series. The present communication deals with the preparation of *bis*-9:10-phenanthrathiophene-indigo starting from 9-thiolphenanthrene through 9:10-phenanthra-2'-ketodihydrothiophene. It is a dark chocolate dye and dyes cotton in brown shade and this result is in conformity with the previous findings of the author.

Preparation of some indigoid dyes starting from 9-thiolphenanthrene has been described. 9-Thiolphenanthrene and some of its derivatives have been prepared by the author ( *J. Indian Chem. Soc.*, 1941, **18**, 469) with a view to preparing some interesting dyes from the point of view of colour in relation to chemical constitution. Some of these dyes have already been described in part X (*ibid.*, 1942, **19**, 239). The present communication deals with the preparation of 9:10-phenanthra-2'-ketodihydrothiophene and some indigoid dyes derived from it by oxidation and condensation with *o*-diketones, such as phenanthraquinone, acenaphthaquinone and isatin. *bis*-9:10-Phenanthrathiophene-indigo, described in this paper, is a dark, chocolate dye which dyes cotton in brown shade and this result is in conformity with the findings of the author (*Ber.*, 1934, **67**, 1319; 1935, **68**, 1447; 1936, **69**, 2343). The dyes prepared from acenaphthaquinone and isatin produce as usual bright red shades on cotton. Works on similar dyes prepared from other isomeric phenanthrene sulphonic acids, such as 2 and 3 are in progress.

### E X P E R I M E N T A L

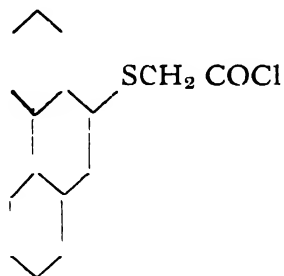
*Phenanthrene-9-thioglycollic Acid,*



9-Thiolphenanthrene (10.5 g.) was dissolved in the required quantity of 10% sodium carbonate solution on a water-bath and to the filtered solution was added monochloroacetic acid (5 g.), previously neutralised with sodium carbonate.

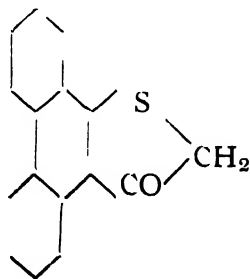
The mixture was heated on a water-bath for half an hour and filtered. The filtrate was then cooled and acidified with hydrochloric acid when the thioglycollic acid separated out as an oil, which after sometime gradually solidified to a white crystalline powder, m.p. 134-35°. (Found : C, 71.23 ; H, 4.6.  $C_{14}H_{12}O_2S$  requires C, 71.64 ; H, 4.47 per cent).

*Phenanthrene-9-thioglycollic Acid Chloride*



The finely powdered, and carefully dried thioglycollic acid (5.36 g.) was suspended in 10 times the quantity of low boiling petroleum ether and then treated with phosphorus pentachloride (4.2 g.). The mixture was then warmed on a water-bath till everything went into a colorless solution. This was cooled in a freezing mixture when the chloride separated out as white crystals which became a sticky mass at ordinary temperature. After the removal of the clear liquid, the mass was subjected to the next operation.

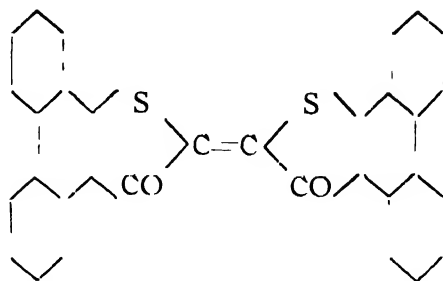
9 : 10-*Phenanthra-2'-ketodihydrothiophene*,



The above sticky chloride without further purification was dissolved in ten times the quantity of low boiling petroleum ether and then cooled to room temperature and next treated slowly with finely powdered anhydrous aluminium chloride (5 g). The mixture was boiled on a water-bath till the evolution of hydrochloric acid ceased. Gradually a red substance was produced. This red substance after the removal of petroleum ether by filtration was decomposed by crushed ice, when a yellowish white sticky mass was obtained. This was dissolved in acetic acid and from the solution it was obtained as yellowish white needles, m p 173-75°. It becomes reddish on exposure to air. It dissolves in caustic soda easily and the solution soon turns green due to oxidation.

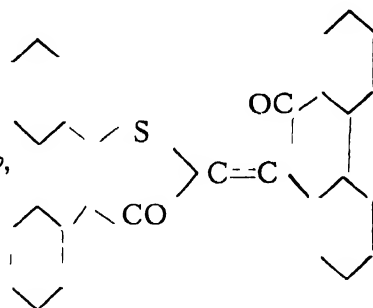
to the *bis*-indigo (Found : C, 76.52 ; H, 4.21.  $C_{16}H_{10}OS$  requires C, 76.80 ; H, 4.4 per cent).

*bis*-9:10-Phenanthrathiophene-indigo,



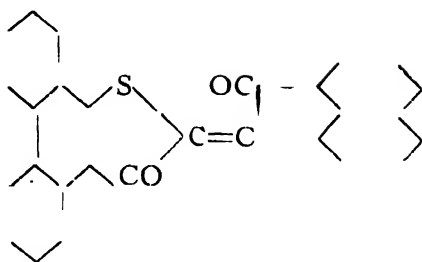
The above oxythiophene (2 g.) was dissolved in 5% dilute caustic soda and an aqueous solution of potassium ferricyanide added until a dark chocolate precipitate was no longer formed. The precipitate was then filtered, and washed with water. It was dissolved in pyridine and from the solution was obtained a chocolate crystalline mass melting above  $280^{\circ}$ . It dissolves in pyridine, nitrobenzene with a dark brown colour and in concentrated sulphuric acid with a chocolate colour. In alkaline hydrosulphite it dissolves with a yellow colour and dyes cotton in brown shade. (Found : C, 77.17 ; H, 3.37.  $C_{12}H_{16}O_2S_2$  requires C, 77.42 ; H, 3.22 per cent).

9 : 10-Phenanthrathiophene-9'-phenanthrene-indigo,



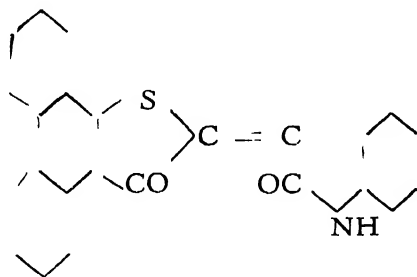
This compound was prepared by heating together phenanthraquinone (1.04 g.), dissolved in 30 c.c. of acetic acid and 9 : 10-phenanthra-2'-ketodihydrothiophene (1.25 g.) in 25 c.c. of acetic acid and adding to the hot solution 0.5 c.c. of hydrochloric acid ( $d$  1.19) when immediately a chocolate precipitate separated out. The mixture was boiled for ten minutes and filtered while hot. The residue was next washed with a little acetic acid and alcohol and crystallised from pyridine in chocolate needles melting above  $280^{\circ}$ . It is fairly soluble in hot pyridine and nitrobenzene and slightly soluble in alcohol and acetic acid. It dissolves in concentrated sulphuric acid with a greenish black colour and in alkaline hydrosulphite with a yellow colour from which it dyes cotton in chocolate-violet shade. (Found : C, 81.51 ; H, 3.81.  $C_{30}H_{16}O_2S$  requires C, 81.82 ; H, 3.63 per cent).

9 : 10-*Phenanthrathiophene-2'-acenaphthylenc-indigo*,



It was prepared in the same way as the previous compound from 9 : 10-phenanthra-2'-ketodihydrothiophene (1.25 g.) and acenaphthaquinone (0.91 g.) in acetic acid solution with traces of hydrochloric acid, and purified in the same manner. From pyridine it separated out as fine, red needles melting above  $280^{\circ}$ . It dissolves in concentrated sulphuric acid with a pale green colour and dissolves in hydrosulphite slightly with a yellowish colour and dyes cotton in beautiful scarlet-red shade. (Found: C, 80.81 ; H, 3.45.  $C_{28}H_{14}O_2S$  requires C, 81.15 ; H, 3.38 per cent).

9 : 10-*Phenanthrathiophene-3'-indol-indigo*,



It was prepared in the same manner as the previous compounds from 9 : 10-phenanthra-2'-ketodihydrothiophene (1.25 g) and isatin ( 0.74 g. ) and purified in the same manner. It was crystallised from nitrobenzene in deep red needles melting above  $280^{\circ}$ . It dissolves in concentrated sulphuric acid with a violet colour and dyes cotton from yellow hydrosulphite vat in red shade. (Found : C, 75.73 ; H, 3.57.  $C_{24}H_{13}O_2NS$  requires C, 75.99 ; H, 3.43 per cent).

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## STRUCTURE OF A BY-PRODUCT OBTAINED DURING THE CLEMMENSEN REDUCTION OF $\beta$ -(*p*-CYMOYL-2)-PROPIONIC ACID

BY SUKH DEV

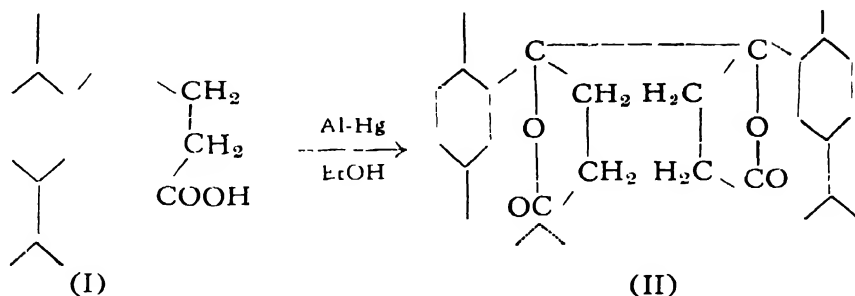
A by-product, m. p. 210-11°, obtained during the Clemmensen reduction of  $\beta$ -(*p*-cymoyl-2)-propionic acid, has been found to be a pinacol-dilactone. The structure has been confirmed by synthesis.

During the synthesis of *apo*-cadalene (Sukh Dev and Guha, this *Journal*, 1948, 25, 14)  $\beta$ -(*p*-cymoyl-2)-propionic acid (I) was subjected to Clemmensen reduction (Martin's procedure). Besides the normal reduction product,  $\gamma$ -(*p*-cymyl-2)-butyric acid, a small amount of a high melting substance was found also to be formed. A number of similar instances have been recorded previously. A solid of m. p. 254° can be isolated as a by-product of the Clemmensen reduction of  $\beta$ -benzoylpropionic acid, for which Fieser has proposed a structure of a pinacol-dilactone ("Organic Syntheses", Vol XV, p. 64). Huang-Minlon (*J. Amer. Chem. Soc.*, 1946, 68, 2487) has also obtained a similar by-product during the Clemmensen reduction (Martin's procedure) of  $\beta$ -(*p*-phenoxybenzoyl)-propionic acid. The production of dimeric substances during the Clemmensen reduction of aromatic ketones is quite common, for example, benzophenone is known to yield dimeric products to the extent of 72-75% ; this problem has been investigated by Bradlow and Vander-Werf (*ibid.*, 1947, 69, 1254).

Fieser (*loc. cit.*) and Huang-Minlon (*loc. cit.*) have provisionally assigned a structure of a pinacol-dilactone for their by-products, probably, only on the basis of the combustion analysis. The insolubility of our product in hot 20% aqueous caustic potash led us to decide against a lactone structure. A reinvestigation of the substance has, however, revealed that though the product is not attacked by hot aqueous alkali, the lactone ring is easily cleaved by hot alcoholic potassium hydroxide. Molecular weight determinations and analysis indicate a similar structure (II) for this product also.

In order to confirm the structure, the substance has been prepared by a straight-forward method. Newman (*ibid.*, 1940, 62, 1683) has developed a new synthesis of coronene, which involves the important step of pinacol reduction of 7-methyl-1-tetralone. He has discovered a new and efficient reagent in aluminium-mercury and absolute alcohol for effecting such pinacolic reductions. Thomas and Nathan (*ibid.*, 1948, 70, 333) have also successfully employed his method. By using this procedure a pinacol-dilactone has been synthesised

from  $\beta$ -(*p*-cymoyl-2)-propionic acid, which has been found to be identical with the by-product of the Clemmensen reduction in all respects.



In as much as the pinacols can be the by-products of the normal alcoholic reduction of ketones, the production of these substances may have some bearing on the mechanism of Clemmensen reduction of  $\beta$ -aroyl-propionic acids. The formation of pinacol-dilactones may indicate that the monomeric lactones may be the intermediates. In fact,  $\gamma$ -phenylbutyrolactone is known to give about as good a yield of  $\gamma$ -phenylbutyric acid as does  $\beta$ -benzoylpropionic acid (Martin, *ibid.*, 1936, 58, 1440).

#### EXPERIMENTAL

*Clemmensen Reduction of  $\beta$ -(*p*-Cymoyl-2)-propionic Acid: Isolation of the by-product.*—The by-product was isolated in exactly the same way as described by Sukh Dev and Guha (this *Journal*, 1948, 25, 18). By using a slight excess of glacial acetic acid during the reduction, the yield of the by-product can be somewhat increased. This is probably due to the resulting higher concentration of the keto-acid in the acid phase of the reaction mixture which is favourable to dimeric condensations.

The product of m. p.  $210-11^\circ$  on further recrystallisations from 90% acetic acid was obtained in small, silvery white, feathery needles, m. p.  $214-15^\circ$ . (Found: C 77.01; H, 8.0; M. W., 428.  $\text{C}_{24}\text{H}_{34}\text{O}_4$  requires C, 77.41; H, 7.83 per cent. M. W., 434).

*Action of Alcoholic Potash.*—The substance (50 mg.) was added to 5% alcoholic potash (10 c.c.) and the mixture was refluxed for 2 hours, cooled and most of the alcohol was distilled off. The residue was taken up in water (5 c.c.) and the clear solution filtered. The filtrate was concentrated a little and then acidified with dilute hydrochloric acid. The precipitated substance was filtered off, washed with water and recrystallised from acetic acid (90%), m. p.  $214-15^\circ$  (mixed m.p. with the original substance,  $214-15^\circ$ ).

*Pinacolic Reduction of  $\beta$ -(*p*-Cymoyl-2)-propionic Acid.*— $\beta$ -(*p*-Cymoyl-2)-propionic acid (5.0 g.) was dissolved in a mixture of absolute alcohol





(30 c.c.) and thiophene-free benzene (dry, 20 c.c.). Bright aluminium foil, freshly cut into small bits (2.0 g.) and mercuric chloride (0.1g.) were added in quick succession. The mixture was swirled for a few minutes and then refluxed on a steam-bath for 4 hours. More of absolute alcohol (15 c.c.) was then added and the refluxing continued for another 2 hours, after which practically all the aluminium had disappeared and the reaction mixture had become pasty and grey. The reaction was completed by refluxing for 6 hours more. The mixture was cooled, and added on to ice and hydrochloric acid (50 c.c.). Some ether was added and the whole transferred to a separating funnel and shaken vigorously till all the aluminium salts had completely disappeared. The product was extracted with ether (thrice) and the combined ether extracts were washed with dilute hydrochloric acid (once), and finally with water (once). The ether solution was then washed with 5% sodium carbonate solution (thrice) to remove the acidic components which were not further examined. The solvent layer was washed twice with water and finally dried (sodium sulphate). On removal of the solvent, a solid was left which was twice recrystallised from 90% acetic acid. The pinacol-dilactone was obtained in fine, silvery white needles, crystallising in rosettes, m.p. 214-15°. A mixed m.p. with a sample of the Clemmensen reduction by-product remained undepressed.

The author's sincere thanks are due to Prof. Dr. P. C. Guha, for the kind interest he has taken in this investigation.

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## THE REACTION BETWEEN AMMONIUM OXALATE AND IODINE

BY W. V. BHAGWAT, S. G. HARMALKAR AND P. K. BHANDARI

The reaction between ammonium oxalate and iodine has been studied both in light and in dark. The results obtained are similar to those obtained in the case of potassium oxalate and iodine. Thus, in dark the reaction is unimolecular with respect to iodine and ammonium oxalate, but becomes semi-molecular with respect to iodine in light. The dark temperature coefficient is high and has a value of about 5 between temperatures 30° and 60°. The temperature coefficient falls to 3.4 for light reaction. The reaction is retarded by KI and shows photochemical after-effect which increases with the increase in the period of pre-illumination. The relation between intensity and velocity obeys square root relationship and the primary process consists in the atomisation of iodine molecules.

Although the reaction between potassium oxalate and iodine, dissolved in KI, has been studied extensively (Dhar, *Proc. K. Akad. Wetensch. Amsterdam*, 1916, 16, 1097; *J. Chem. Soc.*, 1917, 111, 748; 1923, 123, 1853; *Z. Electrochem.*, 1925, 31, 621; Berthoud and Bellenot, *Helv. Chim. Acta*, 1924, 7, 307; Griffith and a McKeown, *Trans. Faraday Soc.*, 1932, 28, 752; Abel and Hilferding, *Z. physikal. Chem.*, 1935, 172A, 353), yet the reaction between ammonium oxalate and iodine has not been investigated.

### *Dark Reaction*

*Order of Reaction with respect to I<sub>2</sub> dissolved in KI etc.*—As the reaction is very slow at low temperatures, the temperatures used were above 30°. Integration method was used to determine the order of the reaction and it was found that unimolecular formulae gave constant results. The order of reaction with respect to ammonium oxalate was determined by Ostwald's isolation method. It comes out to be 1. Thus, the total order of the reaction is 2. The temperature coefficient of the reaction between 40° and 60° is about 5. The value is much lower than that when K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> is used. It is found in several reactions that ammonium salts have a marked accelerating effect. The temperature coefficient of a reaction is determined by its acceleration, and since ammonium oxalate reaction is quicker at low temperature, its temperature coefficient is consequently smaller than that for K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and I<sub>2</sub> reaction. The reaction is retarded by KI, and the retardation increases with the concentration of KI. The results supporting the above conclusions are summarised below.

TABLE I

$I_2 = 0.000977 M$ .  $KI = 0.00937 M$ . Amm. oxalate  $= 0.166 M$ . Temp.  $= 60^\circ$ .

Time,	$\alpha - x$ .	$k_1 \times 60$ .	$k_1^2 \times 60$ .	$K_0 \times 60$ .
0 mins.	12.7	...	...	..
6	11.0	0.0104	0.0823	0.283
14	9.2	0.0109	0.0757	0.250
21	7.7	0.0103	0.0751	0.238
81	5.6	0.0114	0.0771	0.229

TABLE II

Conc. of oxalate.	$k_1 60^\circ$ .	$k_1 50^\circ$ .	$k_1 40^\circ$ .	$k_1 60^\circ / k_1 50^\circ$ .	$k_1 50^\circ / k_1 40^\circ$ .	Ratio of conc.	Ratio of $k_1 60^\circ$ .
0.166 M (a)	0.0114	0.0022	0.00049	5.18	5.5	$\frac{a}{b} = 2$	1.98
0.0833 (b)	0.0058	0.0012	0.00021	5.28	5.2		
0.0416 (c)	0.0033	0.00066	0.00013	5.0	5.1	$\frac{b}{c} = 2$	1.7

TABLE III

Conc. of ammonium oxalate  $= 0.166 M$ .

Conc. of KI	0.00937 M	0.02437 M	0.03937 M	0.05437 M
$k_1 60$	0.0114	0.0039	0.0028	0.0021

### Energy of Activation

Arrhenius' empirical relation,  $\frac{d \log k}{dt} = \frac{E}{RT^2}$ , gives the value 34850 calories for  $E$ , the energy of activation.

Following Lewis that  $Z$  molecules enter into collision per second and then adopting the simplest possible form of distribution law, the fraction of molecules possessing energies greater than  $E_1$  and  $E_2$  are given by  $e^{-E_1/RT}$  and  $e^{-E_2/RT}$ . The chance therefore that two molecules in collision will be such that the energy of one exceeds  $E_1$ , and the energy of the other exceeds  $E_2$  is  $e^{-E_1/RT} \times e^{-E_2/RT} = e^{-(E_1+E_2)/RT} = e^{-E/RT}$ .

Thus the total number of molecules which collide with a joint energy exceeding  $E$  is  $Ze^{-E/RT}$ , where ' $Z$ ' is the number of collisions per second between the reacting molecules and given by  $\sqrt{2} \pi \sigma^2 \bar{n} n^2$  where  $\sigma$  is the molecular diameter,  $\bar{n}$ , the root mean square velocity and ' $n$ ', the number of molecules per c.c.

Thus, the total number of activated molecules colliding is  $\sqrt{2} \cdot \pi \sigma^2 \times \bar{n} \bar{n}^2 e^{-E/RT}$ .

For molecules which are different we have,  $\pi \sigma^2 n_1 \cdot n_2 e^{-E/RT} \times \sqrt{\bar{n}_1^{-2} \cdot \bar{n}_2^{-2}}$  where  $\bar{n}_1$  and  $\bar{n}_2$  are the root mean square velocities of the corresponding molecules.

Assuming that each collision in which joint energy exceeds  $E$ , results in a chemical change, then the number of molecules per c.c. is

$$\pi \sigma^2 n_1 \cdot n_2 e^{-E/RT} \times \sqrt{\bar{n}_1^{-2} \cdot \bar{n}_2^{-2}}$$

Assuming  $\sigma = 3 \times 10^{-8}$  and  $\sqrt{\bar{n}_1^{-2} \cdot \bar{n}_2^{-2}}$  is of the order of  $3 \times 10^{-4}$  cm. and that  $n_1$  for  $(\text{NH}_4)_2\text{C}_2\text{O}_4$   $0.1666M = 1 \times 10^{20}$ ,  $n_2$  for  $\text{I}_2 = 6 \times 10^{17}$  and  $e^{-E/RT} = e^{-34850/2 \times 833}$  when  $T = 60^\circ$ , we get the number of molecules reacting in one second per. c.c. Thus it is equal to

$$3.14 \times 9 \times 10^{-16} \times 1 \times 10^{20} \times 6 \times 10^{17} \times e^{-52.3} \times 3 \times 10^{-4} = 5 \times 10^{19} \times e^{-52.3} \\ = 5 \times 10^{19} \times 1.2 \times 10^{-19} = 6 \text{ (approxly)}$$

The whole of iodine is used up in about 90 minutes at  $60^\circ$  even in presence of KI. Hence, the number of molecules reacting per c.c.  $= 6 \times 10^{17}$ . The number of molecules therefore reacting actually per second  $= \frac{6 \times 10^{17}}{90 \times 60} = 1.1 \times 10^{15}$

It is clear therefore that the observed rate is far greater than the calculated rate. The reaction therefore suggests chain mechanism.

### Photochemical Reaction

The order of reaction with respect to iodine in light comes out to be one half, while it is one with respect to ammonium oxalate. The temperature coefficient is about 35 for ten degree rise of temperature. The reaction is retarded by KI, but the order of reaction does not change. The relation between intensity and velocity shows a square-root relationship. The results are summarised below.

TABLE IV

Conc. of reactants, same as before. Temp  $= 50^\circ$ .

Time.	$a - x$ .	$k_2 \times 60$ .	$k_0 \times 60$ .	$k_1 \times 60$ .
0 mins.	12.7	—	—	—
35	10.7	0.0166	0.067	0.0021
70	8.85	0.0168	0.056	0.0022
104	7.5	0.0158	0.050	0.0021
139	5.95	0.0161	0.048	0.0023
178	4.7	0.0156	0.044	0.0024

TABLE V

Conc of oxalate,	$k_{\frac{1}{2}}^{50^\circ}$ .	$k_{\frac{1}{2}}^{40^\circ}$ .	$k_{\frac{1}{2}}^{30^\circ}$ .	$k_{\frac{1}{2}} \frac{10}{18}$	Ratio of conc.	Ratio of $k_{\frac{1}{2}}^{50^\circ}$ .
0.1666M (a)	0.0190	0.0062	0.0018	3.1	$a/b=2$	1.8
0.0833 (b)	0.0110	0.0034	0.0018	3.2	$b/c=2$	1.9
0.0416 (c)	0.0032	0.00092	0.00026	3.2		

TABLE VI

Conc. of Am. oxalate = 0.166M. Temp. = 50°.

$k_{\frac{1}{2}}$ Dark	$k_{\frac{1}{2}}$ Distance = $d$	$k_{\frac{1}{2}}$ ( $2d$ )	$k_{\frac{1}{2}}$ ( $3d$ )
0.00030	0.0185	0.0073	0.0052
Ratio of intensity.	Ratio of I.	Ratio of velocity.	
$\frac{3^2}{2^2} = 2.25$	1.5	$\frac{0.0070}{0.0049} = 1.4$	
$\frac{2^2}{1^2} = 4$	2	$\frac{0.0182}{0.0070} = 2.6$	

*Photochemical After-effect*

Dhar and Mukerji (*J. Indian Chem. Soc.*, 1928, 5, 203) have observed that the reaction between potassium oxalate and iodine shows photochemical after-effect. The work has been extended by MacMahon and Lal (*ibid.*, 1940, 17, 429) and they have found that the after-effect rate increases with the length of the period of pre-illumination. Our results with ammonium oxalate and iodine show that it behaves similarly.

TABLE VII

Conc. of Am. oxalate = 0.04165 M. Conc. of  $I_2$  = 0.000937M.  
 Conc. of KI = 0.00937M. Temp. = 50°.

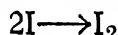
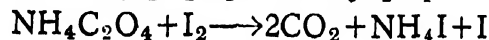
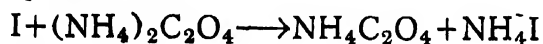
$t_1$ dark.	T.	$k_2$ (exposure, 3 min.).	T.	$k_1$ (exposure, 6 min.).	T.	$k_1$ (exposure, 9 min.).
0.000016	30 min.	0.0000304	20 min.	0.0000604	15 min.	0.0000866
	60	0.0000302	40	0.0000492	30	0.0009776
	90	0.0000279	60	0.0000416	50	0.0000680
	120	0.0000270	100	0.0000333	80	0.000583
	180	0.0000258	150	0.000252	120	0.0000481

The photochemical after-effect falls as the time after cutting off the illumination increases. Our study with different concentrations and temperatures show that after-effect increases as the period of pre-illumination is increased.

### *Mechanism of the Reaction*

In view of the fact that the results obtained with ammonium oxalate and iodine are similar to those obtained in the case of  $K_2C_2O_4$  and  $I_2$ , it suggests itself that the mechanism of the reaction should be similar. We therefore suggest the following mechanism.

It is assumed that primary process is the atomisation of  $I_2$  molecules. Thus,



So that when absorption is complete in total light, we have

$$\frac{d}{dt}(I_2) = k(I_0)^{\frac{1}{2}}[(NH_4)_2C_2O_4]/[I_2]^{\frac{1}{2}}[KI]$$

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## PARACHOR OF IONS

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Parachors of NaCl, KCl, NH<sub>4</sub>Cl, NaNO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub> and KBr at various concentrations have been determined and it is shown that the values obtained are much smaller than those calculated by summing up the parachors of the constituent atoms. It is further shown that Mumford and Phillip's values for ions do not reproduce experimental results for electrolytes in solution.

The atomic parachors of alkali metal as calculated by Sugden from Jaeger's results have been shown to be incorrect.

Mumford's method of calculating ionic parachor from the parachor of fused salts is not correct as at the temperatures mentioned the salts may not have been wholly in the ionic state. Further, according to Born there should be a fixed ratio between the parachors of ions and atoms of the same group and the value should be less than unity. The values as calculated from fused salts do not give this ratio a constant value for alkali metals, although the ratio is less than 1 as is expected.

The method of calculating atomic parachors from the solutions of electrolytes is shown to be incorrect, since electrolytes exist in solution as ions and not as atoms. An expression,

$$P_1 + P_2 = P_m = \frac{(1-x)P_p + (1-x)P_a}{\alpha x}$$

has been derived for calculating the sum of the ionic parachors and has been applied to K<sub>2</sub>CO<sub>3</sub>, KI, NH<sub>4</sub>NO<sub>3</sub>, KCl, NaCl and NH<sub>4</sub>Cl with fairly constant results. Further, it is shown that  $P_1 + P_2$  (ionic) is different from the sum of the atomic parachors. Thus it is shown that ions have fixed parachors which are different from those of atoms. This view is supported further from Ray's results.

Ray (*J. Indian Chem. Soc.*, 1938, 15, 43) and Lakhani and Daroga (*ibid.*, 1938, 15, 37, 519, 604) have determined the parachors of some electrolytes in aqueous solutions. Lakhani and Daroga (*loc. cit.*) had no clear conception of that the values obtained were for ions and not for atoms. Hence they made an attempt to evaluate atomic parachors from the values obtained for electrolytes. Further, they found that the formula

$$P_m = (1-x)I + xP_a$$

was not applicable, and hence tried to suggest a modification. All this confusion was due to the fact that they did not realise that the values obtained were for compounds in the ionised state.

Ray (*loc. cit.*) and Bhagwat and Toshniwal (*J. Indian Chem. Soc.*, 1942, 19, 192; 1944, 21, 53, 61) have shown that the parachor of an electrolyte is different from that of the sum of the constituent atoms. In other words, atomic and ionic parachors are not identical. Further, the value varies with dilution. We have extended this work and our results for some salts are given in the following table.

TABLE I

Substance	$\alpha$ .	$P_x$ at			
		25°.	30°.	40°.	50°.
I. $K_2CO_3$	0.0609	143.6	143.4	140.8	140.6
	0.0723	148.7	147.3	146.9	145.5
	0.0869	156.3	154.5	153.3	153.3
	0.0935	159.0	158.2	158.0	158.0
	0.1125	163.4	162.4	162.0	162.3
	0.1209	169.3	168.8	168.1	167.8
		$P_x$ at			
		20°.	30°.	40°.	50°.
II. KCl	0.0281	101.2	98.7	101.2	96.7
	0.0405	102.5	102.2	100.4	100.7
	0.0570	103.1	103.1	101.2	101.4
III. NaCl	0.0329	70.8	67.5	67.9	68.1
	0.0514	74.5	74.5	73.7	72.7
	0.0712	76.8	76.3	75.6	76.1
	0.0930	77.5	76.4	76.5	75.8
IV. $NH_4Cl$	0.0365	...	123.5	120.5	121.1
	0.0647	...	125.3	125.9	122.2
	0.1020	...	128.1	128.6	127.3
V. $NaNO_3$	0.0230	77.82	85.65	85.48	83.0
	0.0506	94.2	96.6	95.6	95
	0.0836	105.5	106.3	108.2	107.5
		$P_x$ at			
		25°.	30°.	40°.	50°.
VI. KBr	0.0164	114.6	117.6	116.4	...
	0.0364	118.9	114.5	120.3	123.1
	0.0609	116.4	121.0	122.6	120.3

Unfortunately the values for atomic parachor of sodium and potassium from covalent compounds are unknown. If, however, we consider the values  $Na=80$  and  $K=110$ , as given by Sugden, the values for  $K_2CO_3$ ,  $NaCl$ ,  $NH_4Cl$ ,  $KCl$ ,  $KI$ ,  $NH_4NO_3$ ,  $KBr$  and  $NaNO_3$  will be 283.2, 134.3, 135.2, 164.3, 201, 175, 178 and 174.1 respectively. The observed values are much lower than these. In case of ammonium nitrate and chloride, the values for the constituent atoms are known from covalent compounds, and hence there is no doubt that the ionic and atomic parachors are different.

#### DISCUSSION

Sugden and Wilkins (*J. Chem. Soc.*, 1929, 1291) have used surface tensions of fused salts determined by Jaeger (*Z. anorg. Chem.*, 1917, 101, 1) at various temperatures to determine the atomic parachors of alkali metals. In the opinion of the present authors, the work at these high temperatures is not trustworthy. A single case of salts of lithium will illustrate this.



TABLE II

Salt.	Temp.	Parachor.	Mean $P$ .	$\Sigma P$ .	Atomic $P_{Li}$
LiF	850°–1000°	57.8–59.3	58.5	24.1	34.4
LiCl	600°–775°	97.2–99.6	98.4	52.7	45.7
LiNO <sub>3</sub>	350°–500°	130–132.9	131.5	91.5	40.0
Li <sub>2</sub> SO <sub>4</sub>	860°–1160°	212–220	216.0	121.8	2 × 47.1

The mean of these values is not 50 which is taken as the atomic parachor of Li. The selection by Sugden is purely arbitrary not only in this case but same is true for his values of atomic parachors of Na, K, Rb and Cs. Mumford and Phillips (*J. Chem. Soc.*, 1929, 2130) object to the use of one and the same atomic constant for the combined atom and for the ion of an element, by Sugden and Wilkins (*loc. cit.*). They believe that at these high temperatures and in fused state the salt ionises and the ions and not the atoms are existing.

If in accordance with the views of Born (*Z. Physik*, 1920, 1, 45) the volume measured by the parachor is regarded as being directly and simply related to the actual dimensions of the molecule or atom concerned (cf. Sugden, *J. Chem. Soc.*, 1929, 1055), then the parachor values of the ions of the halogens may be approximately estimated from the atomic parachors of rare gases which follow them in periodic classification. Calculation on this basis (Pauling, *J. Amer. Chem. Soc.*, 1927, 49, 465) indicates that the parachor values of halide ions should on an average be 1.46 times those of the atoms of the corresponding rare gases, and hence about 1.44 times those of the halogen atoms in non-polar combination. The approximate ionic parachors obtained by this method are  $F' = 36$ ,  $Cl' = 79$ ,  $Br' = 99$ ,  $I' = 130$ . When these values are subtracted from the observed parachors of the fused alkali metal salts, the ionic parachors of these alkali metals are obtained. Thus, we have  $Li = 21$ ,  $Na = 45$ ,  $K = 76$ ,  $Rb = 95$  and  $Cs = 109$ . On similar lines the parachor values for  $NO_3'$ ,  $PO_3'$  and  $SO_4''$  ions are obtained. Thus,  $NO_3' = 109$ ,  $PO_3' = 132$  and  $SO_4'' = 172$ . This procedure of calculating ionic parachor from the observed values of the parachors of fused salts is in the opinion of the authors highly objectionable, since the parachor values at these high temperatures are not accurate. A rough idea of this variation will be obtained from the following table.

TABLE III

Salt.	Parachor.	Salt.	Parachor.
Li <sub>2</sub> SO <sub>4</sub>	212.4–220.6	NaNO <sub>3</sub>	147.9–158.4
Na <sub>2</sub> SO <sub>4</sub>	257.5–265.8	KNO <sub>3</sub>	184.2–193.6
K <sub>2</sub> SO <sub>4</sub>	319.5–336.5	RbNO <sub>3</sub>	192.5–203.7
Rb <sub>2</sub> SO <sub>4</sub>	356.9–368.1	Cs <sub>2</sub> SO <sub>4</sub>	386.8–393.1

Secondly, it is assumed that in fused state at the temperature range examined, the salts ionise completely. No evidence has been produced to show

that ionisation is not partial but complete in all cases. Thirdly, just as the ionic parachors of halide ions are on average  $x$  times (1.44) the parachor of corresponding atom, so the parachor value of ions of alkali metal should also be  $m$  [ $m$  should be less than unity since according to Born (*loc. cit.*) positive ions have smaller volume than the corresponding atoms) times the atomic parachor of the corresponding atom. - The ratio of ionic parachor as calculated above and of atomic parachor by Sugden is as follows

TABLE IV

Element.	$P_{\text{ion.}}$	$P_{\text{atom.}}$	Ratio, $m = \frac{P_{\text{ion.}}}{P_{\text{atom.}}}$	Group.	$P_{\text{ion.}}$	$P_{\text{atom.}}$	$m$ .
Na	45	80	0.56	$\text{NO}_3'$	109	94.1	1.16
K	76	110	0.69	$\text{PO}_3''$	132	119.3	1.10
Li	21	50	0.42	$\text{SO}_4'''$	172	125	1.33
Rb	95	130	0.73				
Cs	109	150	0.73				

The results with alkali metals show that the value of  $m$  varies appreciably. The ions  $\text{NO}_3'$  and  $\text{PO}_3'$  are similar in structure and the values of  $m$  in two cases agree appreciably. Fortunately here, the values of atomic parachor of N, O, P and S are known directly from covalent compounds. The values for parachors of NaCl,  $\text{NaNO}_3$ , KI, KBr and KCl, as calculated from the results of Mumford and Phillip, are 124, 154, 206, 175 and 153 respectively. The observed values in solution are much smaller than these. Thus Mumford and Phillip's values fail to reproduce experimental results.

It will be clear from the above discussion that no reliable values of ionic parachor even for thermal ionisation are known.

Lakhani and Daroga (*J. Indian Chem. Soc.*, 1938, 15, 37) were the first to study the parachor of inorganic salts, but it seems that they were not aware of the work of Mumford and Phillip (*loc. cit.*) on the parachor of ions in fused state. They therefore wrongly tried to determine the atomic parachors of metallic elements from the parachor of salts which ionise in aqueous solutions (*ibid.*, 1938, 15, 604, 37, 519).

Toshniwal (thesis submitted to Agra University, 1945) has tried to show that ions have specific parachor values by considering the salts at equimolecular concentrations, assuming that they ionise equally at these concentrations. He did not attempt to calculate the actual values of individual ions, but applied Kohlrausch principle of mobilities of ions that as strong electrolytes ionise completely  $P_{\text{NaCl}} - P_{\text{KCl}} = P_{\text{NaNO}_3} - P_{\text{KNO}_3}$ . He showed that approximately constant results were obtained. The work therefore is incomplete. In this paper we have attempted to show that ions have definite parachor values by showing that sum of ionic parachor at different dilutions is constant, taking into consideration the degrees of ionisation as obtained from the corresponding

values of  $\mu_v/\mu^\infty$  and applying the viscosity correction. These results are available from the Standard Tables.

Hence, values for such salts alone are calculated from the results given by us in previous pages, for which  $\mu_v/\mu^\infty$  and viscosity data are available.

The following expression is derived by us for determining the ionic parachor.

Let the molecular fraction of the electrolyte (binary) and of the solvent in a solution be  $x$  and  $1-x$  respectively. Let  $\alpha$  be the degree of ionisation of the salt in this solution. Let  $M_p$  be the molecular weight of the solvent,  $M_s$ , the molecular weight of the salt and  $M_1$  and  $M_2$  be the weights of cation and anion, such that  $M_s = M_1 + M_2$ . The number of ions of each kind present in the solution is thus  $\alpha x$  and the number of molecules of solute left is  $(1-\alpha)x$ . The total number of individuals in solution is now

$$= 1-x \text{ (of solvent)} + (1-\alpha)x \text{ of the salt} + \alpha x \text{ of cations} + \alpha x \text{ of anions} \\ = 1 + \alpha x.$$

$$\text{Hence the molar fraction of the solvent} = \frac{1-x}{1+\alpha x}$$

$$\text{,, undissociated molecules of salt} = \frac{(1-\alpha)x}{1+\alpha x}$$

$$\text{,, each ion} = \frac{\alpha x}{1+\alpha x} \text{ cation} \\ \frac{\alpha x}{1+\alpha x} \text{ anion}$$

Thus the mean molecular weight

$$M_3 = \frac{(1-x)M_p}{1+\alpha x} + \frac{(1-\alpha)xM_s}{1+\alpha x} + \frac{\alpha x M_1}{1+\alpha x} + \frac{\alpha x M_2}{1+\alpha x}$$

$$\text{or } (1+\alpha x)M_3 = (1-x)M_p + (1-\alpha)xM_s + \alpha x M_1 + \alpha x M_2 \\ = (1-x)M_p + (1-\alpha)xM_s + \alpha x(M_1 + M_2)$$

$$\text{But } M_1 + M_2 = M_s$$

$$\text{Hence } (1+\alpha x)M_3 = (1-x)M_p + xM_s$$

But by Hammick and Andrew's equation

$$M_m = (1-x)M_p + xM_s$$

$$\text{Hence } (1+\alpha x)M_3 = M_m$$

The parachor of the solution is given by :

$$P_s = \frac{M_3 r^{\frac{1}{4}}}{d} = \frac{M_m}{(1+\alpha x)d} r^{\frac{1}{4}}$$

$$\text{But } P_m = \frac{M_m r^{\frac{1}{4}}}{d} \text{ or } P_s(1+\alpha x) = P_m$$

$$\text{Also, } P_s = \frac{1-x}{1+\alpha x} P_p + \frac{(1-\alpha)x}{1+\alpha x} P_s + \frac{\alpha x}{1+\alpha x} P_1 + \frac{\alpha x}{1+\alpha x} P_2$$

$$\text{or } (1+\alpha x)P_s = (1-x)P_p + (1-\alpha)xP_s + \alpha x(P_1 + P_2)$$

$$\text{or } P_m = (1-x)P_p + (1-\alpha)xP_s + \alpha x(P_1 + P_2)$$

$$\text{or } P_1 + P_2 = \frac{P_m - \{(1-x)P_p + (1-\alpha)xP_s\}}{\alpha x}$$

For  $P_*$ , the parachor of undissociated molecules of the salt, the values given by Sugden are used. The results will show that the sum of ionic parachors is less than that for undissociated molecules, indicating that ions and molecules have different parachor constants. Further, although varying concentrations are used, the result for sum of ionic parachors is practically constant, showing that ions have fixed parachor constants. The results have also been calculated from Ray's observations (*loc. cit.*). In all cases the constancy is fair considering the fact that molar fractions in all cases are low, as the amount that can be dissolved at a fixed temperature is fixed by the solubility of the salt. The results of Ray are not identical with those of ours; they are, however, among themselves constant. The variation is due to the fact that a slight variation in  $P_m$  has an immense effect on the final calculation, since molar fractions of the salt are low. The molar fraction varies from  $M/100$  to  $M/10$  and therefore the error present in  $P_m$  may be magnified from 10 to 100 times in calculating  $P_1 + P_2$ .

TABLE V

NH<sub>4</sub>Cl.

$x$ .	$\mu v$ .	$\mu \infty$ .	$\mu v/\mu \infty$ .	$\eta v/\eta \infty$ .	$\alpha$ .	NH <sub>4</sub> <sup>+</sup> + Cl <sup>-</sup> .
0.0365	92.4		0.7636	0.9730	0.7429	125.7
0.0567	88.4	121.0	0.7305	0.9703	0.7088	123.1
0.1020	80.5		0.6619	0.9642	0.6429	122.0

The value for (NH<sub>4</sub> + Cl<sup>-</sup>) from Ray's results (*J. Indian Chem. Soc.*, 1938, 15 44) varies from 105—112 when  $x$  varies from 0.017 to 0.099.

## KI.

$x$ .	$\mu v$ .	$\mu \infty$ .	$\mu v/\mu \infty$ .	$\eta v/\eta \infty$ .	$\alpha$ .	K <sup>+</sup> + Cl <sup>-</sup> .
0.0325	102.2		0.7861	0.921	0.7130	129.7
0.0491	98.8	130.27	0.7600	0.9178	0.6869	130.8
0.0789	90.0		0.6923	0.9150	0.6238	127.2
0.0989	83.7		0.6438	0.9124	0.5794	125.5

Values calculated from Ray's results for (K<sup>+</sup> + Cl<sup>-</sup>) vary from 100 to 109 when  $x$  varies from 0.041 to 0.086.

K<sub>2</sub>CO<sub>3</sub>.2K<sup>+</sup> + CO<sub>3</sub><sup>2-</sup>

0.0609	35.1		0.2815	2.3815	0.6704	74.2
0.0723	29.86	124.8	0.2315	2.7707	0.6414	69.8
0.1209	13.0		0.1043	5.4808	0.5616	79.1
0.1125	14.08		0.1127	4.6992	0.5296	59.0
0.0935	20.71		0.1603	3.8292	0.6368	86.8
	23.54		0.1888	3.8853	0.6891	83.1

TABLE V

$x$ .	$\mu\theta$ .	$\mu\infty$ .	KCl		$\alpha$ .	K <sup>+</sup> +Cl <sup>-</sup> .
			$\mu/\mu\infty$ .	$\eta/\eta\infty$ .		
0.0261	95.2		0.7323	0.9967	0.7225	76.9
0.0406	91.5	130.11	0.7038	0.9969	0.7038	76.0
0.05703	88.9		0.6823	1.011	0.6913	75.8
0.01822	98.22		0.7554	0.982	0.7420	75.2

Values calculated from Rays' results vary from 81 to 85 when  $x$  varies from 0.01 to 0.04.

NH<sub>4</sub>NO<sub>3</sub>.NH<sub>4</sub><sup>+</sup>+NO<sub>3</sub><sup>-</sup>.

0.0243	85.9		0.7320	1.1180	0.8403	148.6
0.0535	76.0	117.34	0.6477	1.1319	0.7331	154.0
0.0880	67.1		0.5718	1.1725	0.6703	146.4

Values calculated from Ray's results vary from 140 to 155 as  $x$  varies from 0.01 to 0.18.

## NaCl.

 $P_{\text{fused}} = 124.8$ Na<sup>+</sup>+Cl<sup>-</sup>.

0.3289	66.2		0.6073	1.1559	0.702	43.8
0.0514	57.8		0.5303	1.2126	0.659	40.9
0.7127	49.9	108.99	0.4578	1.3111	0.614	40.7
0.0180	74.31		0.6917	1.0568	0.711	40.9

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PHYSICO-CHEMICAL STUDIES ON THE COMPOSITION OF  
COMPLEX METALLIC FERRO AND FERRICYANIDES  
PART VIII. THERMOMETRIC STUDY OF THE  
COMPOSITION OF CADMIUM FERRICYANIDE

BY HARISH C. GAUR AND ABANI K. BHATTACHARYA

The composition of cadmium ferricyanide has been studied by the thermometric titrations of cadmium sulphate solutions with  $K_3FeCy_6$  solutions, both by direct and reverse methods, in aqueous and aqueous alcoholic media. The results support the constitution of the compound as  $KCd_{10} (Fe^{III} Cy_6)_7$ , arrived at earlier by the conductometric method.

Studies on the composition of cadmium ferricyanide have been further extended. The thermometric studies support the results of the conductometric studies (this *Journal*, 1948, 25, 349). The compound  $KCd_{10} (Fe^{III} Cy_6)_7$  is formed, but the composition is also influenced by hydrolysis and adsorption.

EXPERIMENTAL

'AnalaR' (B. D. H.) reagents were used. Preparation of the standard solution has been described in Part VII (*loc. cit.*). The thermometric titration arrangement was similar to the one used previously (this *Journal*, 1947, 24, 487 ; 1948, 25, 185). With different concentration of the two salt solutions, the titrations were carried out by the direct and the reverse methods, *i.e.*, when cadmium sulphate from the burette was added to potassium ferricyanide taken in the thermos flask, and *vice versa*. The titrations were also carried out in presence of alcohol up to a total concentration of 20% by volume.

$M/4.82$  solution of cadmium sulphate would be referred as A/1-solution of cadmium sulphate, and  $M/5.06$  solution of potassium ferricyanide as A/1- $K_3FeCy_6$  solution.

Control experiments, as communicated in part VII (*loc. cit.*) of this series, showed that inspite of its oxidising nature, potassium ferricyanide had no action on alcohol under the conditions of the experiment. Hence the titre values do not suffer any change due to this.

*Direct Thermometric Titrations*

TABLE I

A/10-K<sub>3</sub>FeCy<sub>6</sub> = 20 c. c.  
Alcohol = nil (curve 1).

A/1-CdSO <sub>4</sub> added.	Total rise in temp.
0.4 c.c.	0.035°
0.8	0.065
1.6	0.125
2.4	0.195
3.2	0.255
4.0	0.290°
4.8	0.325

TABLE II

A/10-K<sub>3</sub>FeCy<sub>6</sub> = 18 c.c. ·  
Alcohol = 2 c. c. (curve 2).

A/1-CdSO <sub>4</sub> added.	Total rise in temp.
0.2 c.c.	0.020°
0.8	0.080
1.4	0.140
1.8	0.175
2.0	0.200
2.4	0.240
3.2	0.280

TABLE III

A/10-K<sub>3</sub>FeCy<sub>6</sub> = 16 c.c.  
Alcohol = 4 c.c. (curve 3).

A/1-CdSO <sub>4</sub> added.	Total rise in temp.
0.2 c.c.	0.025°
0.4	0.050
0.8	0.095
1.4	0.185
1.8	0.245
2.2	0.305
2.8	0.365

TABLE IV

A/10-K<sub>3</sub>FeCy<sub>6</sub> = 20 c.c.  
Alcohol = nil (curve 4).

A/2-CdSO <sub>4</sub> added.	Total rise in temp.
0.4 c.c.	0.030°
1.2	0.070
1.6	0.100
2.4	0.160
3.6	0.245
4.4	0.310
5.2	0.365
6.4	0.430

TABLE V

A/10-K<sub>3</sub>FeCy<sub>6</sub> = 18 c.c.  
Alcohol = 2 c.c. (curve 5).

A/2-CdSO <sub>4</sub> added.	Total rise in temp.
0.4 c.c.	0.015°
1.2	0.045
2.0	0.075
2.8	0.105
3.2	0.120
4.0	0.150
5.2	0.190
6.4	0.220

TABLE VI

A/10 K<sub>3</sub>FeCy<sub>6</sub> = 16 c.c.  
Alcohol = 4 c.c. (curve 6).

A/2-CdSO <sub>4</sub> added.	Total rise in temp.
0.4 c.c.	0.030°
1.2	0.120
2.0	0.205
2.8	0.285
3.2	0.320
4.4	0.425
4.8	0.455°
5.6	0.495

*Reverse Thermometric Titrations*

TABLE VII

A/10-CdSO<sub>4</sub> = 20 c.c.  
Alcohol = nil. (curve 7).

A/2-K <sub>3</sub> FeCy <sub>6</sub> added.	Total rise in temp.
0.2 c.c.	0.010°
0.6	0.040
1.0	0.070
1.4	0.105
1.8	0.140
2.2	0.175
2.6	0.210°
2.8	0.225
3.2	0.245

TABLE VIII

A/10-CdSO<sub>4</sub> = 18 c.c.  
Alcohol = 2 c. c. (curve 8)

A/2-K <sub>3</sub> FeCy <sub>6</sub> added.	Total rise in temp.
0.2 c.c.	0.010°
0.6	0.035
1.0	0.070
1.2	0.085
1.6	0.120
1.8	0.135
2.6	0.200
3.0	0.220
3.2	0.230

TABLE IX

A/10-CdSO<sub>4</sub> = 16 c.c.  
Alcohol = 4 c. c. (curve 9)

A/2-K <sub>3</sub> FeCy <sub>6</sub> added.	Total rise in temp.
0.2 c.c.	0.010°
0.6	0.050
0.8	0.065
1.2	0.100
1.6	0.140
2.0	0.180
2.6	0.220
2.8	0.225°
3.0	0.240

TABLE X

A/10-CdSO<sub>4</sub> = 20 c.c.  
Alcohol = nil (curve 10).

A/4-K <sub>3</sub> FeCy <sub>6</sub> added.	Total rise in temp.
0.4 c.c.	0.010°
0.8	0.025
2.0	0.070
3.2	0.120
4.4	0.170
5.6	0.220
6.4	0.250
6.8	0.260

TABLE XI

A/10-CdSO<sub>4</sub> soln. = 18 c.c.  
Alcohol = 2 c.c. (curve 11).

A/4-K <sub>3</sub> FeCy <sub>6</sub> added.	Total rise in temp.
0.4 c.c.	0.010°
0.8	0.020
2.0	0.060
3.2	0.125
4.4	0.185
5.6	0.235
6.0	0.245
6.4	0.255

TABLE XII

A/10-CdSO<sub>4</sub> soln. = 16 c.c.  
Alcohol = 4 c.c. (curve 12).

A/4-K <sub>3</sub> FeCy <sub>6</sub> added.	Total rise in temp.
0.4 c.c.	0.040°
0.8	0.080
2.0	0.205
3.2	0.315
3.6	0.350
4.8	0.445
5.6	0.495
6.0	0.515

TABLE XIII

*Direct thermometric titrations*

A/1-Cadmium sulphate and A/10-potassium ferricyanide. Conc. ratio (n) = 10 : 1.

A/10-K <sub>3</sub> FeCy <sub>6</sub> in the cell.	Alcohol added.	CdSO <sub>4</sub> reqd. for K <sub>3</sub> FeCy <sub>6</sub> in the cell.	CdSO <sub>4</sub> calc. for 20 c.c. A/10-K <sub>3</sub> FeCy <sub>6</sub>	Equiv. vol of A/10-CdSO <sub>4</sub> .	Curve No
10 c.c.	0.0 c.c.	2.74 c.c.	2.74 c.c.	27.4 c.c.	1
9	1.0	2.44	2.71	27.1	2
8	2.0	2.16	2.70	27.0	3

A/2-Cadmium sulphate and A/10-potassium ferricyanide, Conc. ratio (n) = 5:1.

10	0.0 c.c.	5.52 c.c.	5.52 c.c.	27.60 c.c.	4
9	1.0	4.92	5.47	27.35	5
8	2.0	4.32	5.40	27.00	6

*Reverse thermometric titrations*

A/2-Potassium ferricyanide and A/10-cadmium sulphate. Conc. ratio (n) = 5:1.

A/10-CdSO <sub>4</sub> in the cell.	Alcohol added.	K <sub>3</sub> FeCy <sub>6</sub> reqd. for CdSO <sub>4</sub> in the cell	K <sub>3</sub> FeCy <sub>6</sub> calc. for 20 c.c. of A/10-CdSO <sub>4</sub> .	Equiv. vol. of A/10-K <sub>3</sub> FeCy <sub>6</sub> .	Curve No.
Conc. ratio (n) = 5 : 1.					
10 c.c.	0.0 c.c.	2.74 c.c.	2.74 c.c.	13.7 c.c.	7
9	1.0	2.52	2.80	14.0	8
8	2.0	2.32	2.90	14.5	9

A/4-Potassium ferricyanide and A/10 cadmium sulphate Conc. ratio (n) = 2.5 : 1.

10 c.c.	0.0 c.c.	5.48 c.c.	5.48 c.c.	13.7 c.c.	10
9	1.0	5.00	5.56	13.9	11
8	2.0	4.64	5.80	14.5	12



## DISCUSSION

In continuation of our previous studies on the composition of cadmium ferricyanide by the conductometric method (Part VII, *loc. cit.*), the thermometric study of the compound has been carried out. The nature of the discrepancies between the theoretical and observed titre values, in the aqueous and aqueous-alcoholic media in the direct and reverse titrations are similar.

FIG. 1

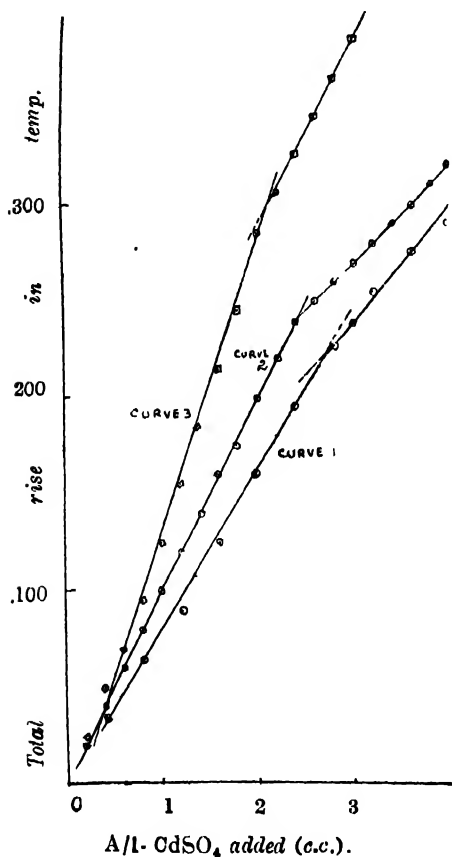
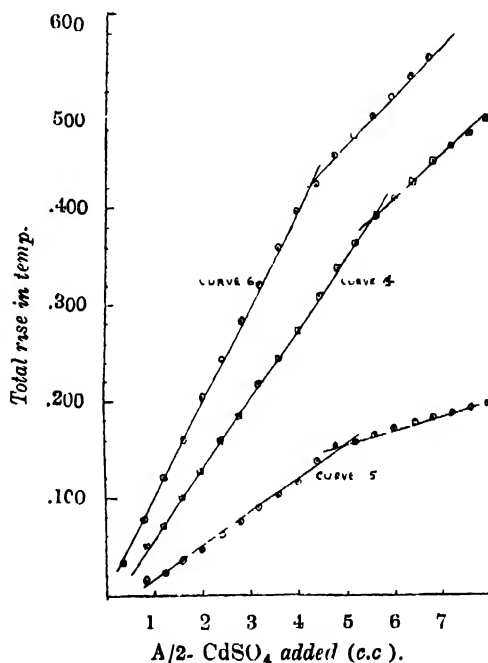


FIG. 2

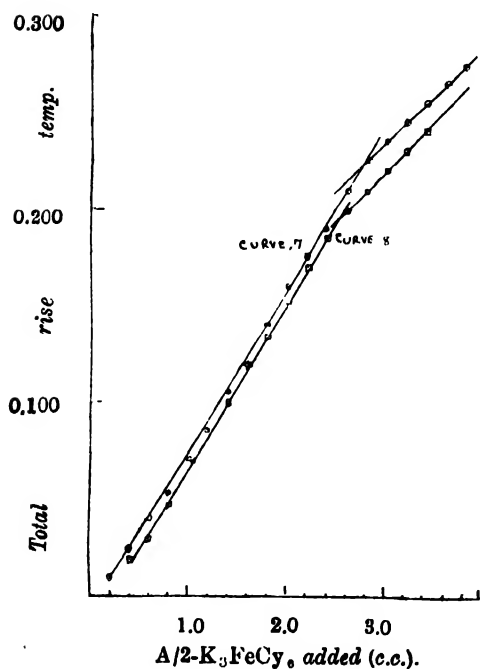


From the strengths of the solutions of cadmium sulphate ( $M/4.82$ ), and potassium ferricyanide ( $M/5.06$ ), the theoretical titre values for 20 c.c. of potassium ferricyanide solution for the formation of the compounds  $\text{KCd}(\text{Fe}^{\text{III}}\text{Cy}_6)$ ,  $\text{Cd}_3^+(\text{Fe}^{\text{III}}\text{Cy}_6)_2$  and  $\text{KCd}_{10}(\text{Fe}^{\text{III}}\text{Cy}_6)_7$ , in the direct titration are 19.04, 28.5 and 27.1 c.c. of cadmium sulphate solution respectively. The theoretical titre values for 20 c.c. of cadmium sulphate solution for the formation of the same compounds in the reverse titrations are respectively 21.0, 14.04 and 14.74 c.c. of potassium ferricyanide solution.

The observed titre values for 20 c.c. of potassium ferricyanide solution in aqueous medium is 27.4 to 27.6 c.c. of cadmium sulphate solution, which, in presence of increasing amounts of alcohol, decreases and very nearly approaches the theoretical<sup>1</sup> titre value required for the formation of the compound  $\text{KCd}_{10}(\text{Fe}^{\text{III}}\text{Cy}_6)_7$ . Taking into consideration the hydrolysability of such compounds, as has already been observed (Part VII), the titre values in direct titrations in aqueous medium would be slightly higher than the theoretical titre value. In presence of increasing amounts of alcohol, the titre values would decrease, as the hydrolysis would be checked to some extent. The observed titre values then in aqueous-alcoholic medium would approach the theoretical titre value for the complex which is actually formed. From this consideration it is obvious that the compound  $\text{Cd}_3(\text{Fe}^{\text{III}}\text{Cy}_6)_2$  is not formed as the observed titre value in presence of increasing amounts of alcohol recedes further from the theoretical titre value. The values, on the other hand, support the formation of the compound  $\text{KCd}_{10}(\text{Fe}^{\text{III}}\text{Cy}_6)_7$ .

From the view point of hydrolysis, the observed titre values in aqueous medium in case of reverse titrations would be lower than the theoretical one, and in presence of increasing amounts of alcohol they would gradually increase, and approach the theoretical value required for the formation of the complex. This is actually observed (Table XIII), and the observations strongly support the formation of the complex  $\text{KCd}_{10}(\text{Fe}^{\text{III}}\text{Cy}_6)_7$ .

FIG 3



0,300

FIG 4

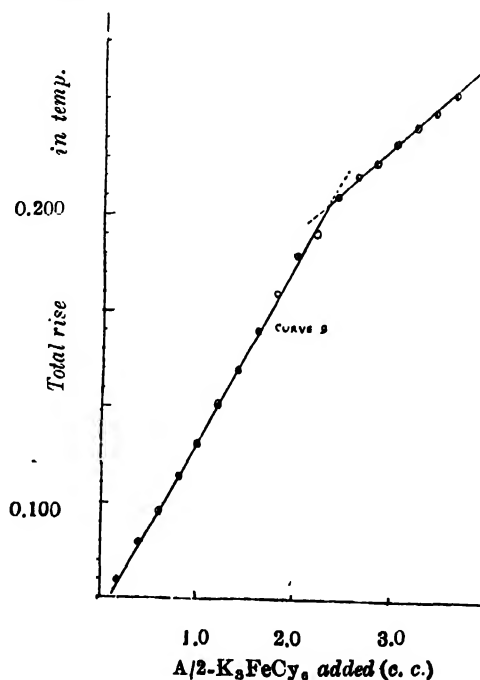


FIG. 5

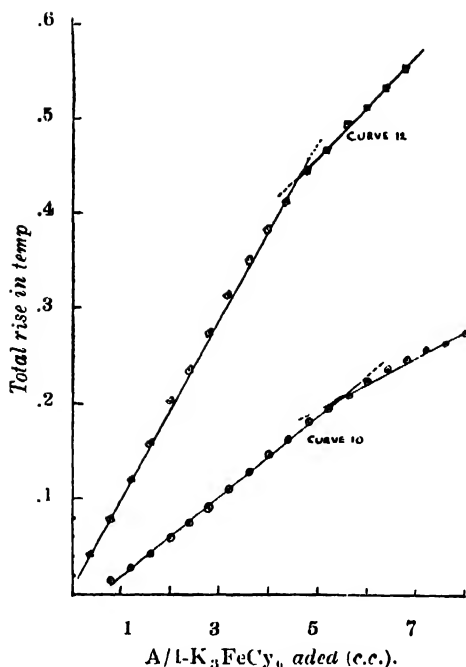
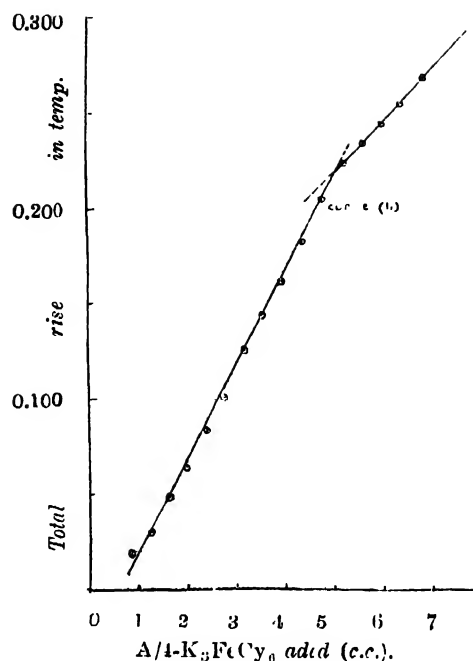


FIG. 6



It is further observed that the discrepancy between the observed and theoretical titre values for the formation of the compound  $\text{KCd}_{10}(\text{Fe}^{\text{III}}\text{Cy}_6)_7$  is, in general, much less than what had been observed in the case of cadmium ferrocyanide (Part IV, *loc. cit.*). Ferricyanic acid is a stronger acid than ferrocyanic acid and hence metallic ferricyanides will, as a rule, be much less hydrolysable than the corresponding ferrocyanides. This is revealed in Table XIII when the theoretical and observed titre values become almost identical in aqueous-alcoholic medium.

The adsorption of  $\text{Cd}^{++}$  and  $(\text{FeCy}_6)^{--}$  ions by the precipitated complex would also affect the theoretical titre values. In the reverse titrations cadmium sulphate being in the thermos flask, the titrations are carried out in presence of excess of cadmium sulphate, and hence the chances of adsorption of  $\text{Cd}^{++}$  ions are greater. Therefore, its effect in aqueous medium would be to lower the observed titre values; and in presence of increasing amounts of alcohol a slight increase in the observed titre values will take place, because of less adsorption in the aqueous-alcoholic medium. This has been actually observed. (Table XIII). In the direct titrations the chances of adsorption of  $(\text{FeCy}_6)^{--}$  are greater than  $\text{Cd}^{++}$  ions, and hence the observed titre values should be lower than the theoretical one. But experimentally the titre values of cadmium sulphate observed are 27.4 to 27.6 c. c. as against 27.1 c. c. [theoretical

value for the formation of the compound  $\text{KCd}_{10}(\text{Fe}^{\text{III}}\text{Cy}_6)_7$ . From the specific nature of the adsorptive properties it may be possible that  $\text{Cd}^{++}$  ions are adsorbed more than  $(\text{FeCy}_6)^{+++}$  ions, and thus the discrepancy of the titre values can be explained.

The experiments on hydrolysis and adsorption are in progress, and will be communicated in a later issue.

Thus, on the basis of the thermometric and conductometric results conclusive evidence for the formation of the compound  $\text{KCd}_{10}(\text{Fe}^{\text{III}}\text{Cy}_6)_7$  is obtained.

Thanks of the authors are due to Dr. S. S. Deshapande for his kind interest in the progress of this work, and also to Dr. K. C. Mehta, Principal Agra College, for the grant of a Research Fellowship to one of the authors (H. C. Gaur).

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## ON ORGANO-ARSENICAL COMPOUNDS. PART II

BY B. PATHAK AND T. N. GHOSH

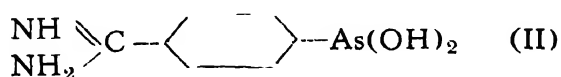
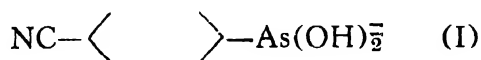
Synthesis of *para*-amidinophenylarsenious acid is described.

Although filarial infections are widely distributed in the tropics, no potent and dependable filaricide has yet been discovered. Recently, promising results in the chemotherapy of filariasis have been obtained with some phenylarsenoxide derivatives by Otto and Maren (*Science*, 1947, **106**, 105). In course of this investigation, they have found *p*-arsenobenzamide, and specially, *p*-[bis-(carboxy-methylmercapto)-arsino]-benzamide quite active on animal tests. The latter compound has been found to kill all the adults of *D. immitis* in doses which appear to be feasible for man. In view of the recent observations on the pronounced parasitocidal properties of various amidine derivatives (King, Lourie and Yorke, *Ann. Trop. Med. Parasitol.*, 1937, **233**, 136; Ashley, Barber, Ewins, Newbery and Self, *J. Chem. Soc.*, 1942, 103; Kirk and Sati, *Ann. Trop. Med. Parasitol.*, 1940, **34**, 82; Adams and Yorke, *ibid.*, 1939, **33**, 323; 1940, **34**, 174), it has been considered desirable and rational to synthesise *p*-amidinophenylarsenoxide and its derivatives, so that these compounds may be tested for any filaricidal activity.

*p*-Amidinophenylarsenoxide could not be successfully prepared from *p*-amidinophenylarsonic acid (Linsker and Bogert, *J. Amer. Chem. Soc.*, 1943, **65**, 932) by reduction with sodium bisulphite (compare Doak, Steinman and Eagle, *J. Amer. Chem. Soc.*, 1940, **62**, 3013) of the sodium salt of the arsonic acid in aqueous solution or by reduction of the arsonic acid in dilute sulphuric acid solution with sulphur dioxide in presence of a trace of potassium iodide (D. R. P., 235391).

*p*-Cyanophenylarsenious acid (I), which has now been prepared by reduction of the aqueous solution of the sodium salt of *p*-cyanophenylarsonic acid (Linsker and Bogert, *loc. cit.*) with sodium bisulphite, has been smoothly converted into *p*-amidinophenylarsenious acid (II), via the corresponding imino-ether hydrochloride.

The compound (II) yields a crystalline hydrochloride, which is under pharmacological examination.



## EXPERIMENTAL

*p*-Cyanophenylarsenious Acid (I).—*p*-Cyanophenylarsonic acid (prepared according to the method of Linsker and Bogert, *loc. cit.*, 23 g.) was dissolved in 5% caustic soda solution (80 c. c.) at room temperature. The solution

was diluted with water to 150 c. c. and sodium bisulphite (40 g.) then added with shaking. After filtration to remove any suspended impurity, the solution was allowed to stand at ordinary temperature in a chamber free from acid fumes for 12 days with occasional shaking, when gradually a brownish, crystalline solid was precipitated. The solid was filtered, washed with cold water, triturated with dilute aqueous ammonia, filtered and finally washed thoroughly with water, yield 14 g. It is soluble in cold dilute alkali but insoluble in aqueous ammonia or sodium bicarbonate. It is sparingly soluble in hot water and in alcohol and could not be recrystallised from these solvents. It was, however, purified by solution in dilute alkali and precipitation, under cooling, with hydrochloric acid, and was dried *in vacuo* over fused calcium chloride. It softens at 239° and melts at 253–55° to a viscous liquid. (Found : N, 6.34 ; As, 35.88.  $C_7H_8O_2NAs$  requires N, 6.63 ; As, 35.51 per cent).

*p-Amidinophenylarsenious Acid* (II).—The above compound (I, 15 g.) was finely powdered and suspended in dry ether (45 c.c.) to which absolute alcohol (6 c.c.) was added. Dry hydrochloric acid gas was then passed into this mixture, kept at 0°. Within a few minutes, a clear solution was obtained and on further passing hydrochloric acid gas till saturated, the solution became turbid. The mixture, kept in a well-stoppered flask, was then left in a refrigerator for 10 days with occasional shaking, when the imino-ether hydrochloride separated as a brownish powder, which was filtered off, washed with dry ether and dried in a vacuum desiccator, yield 10g.

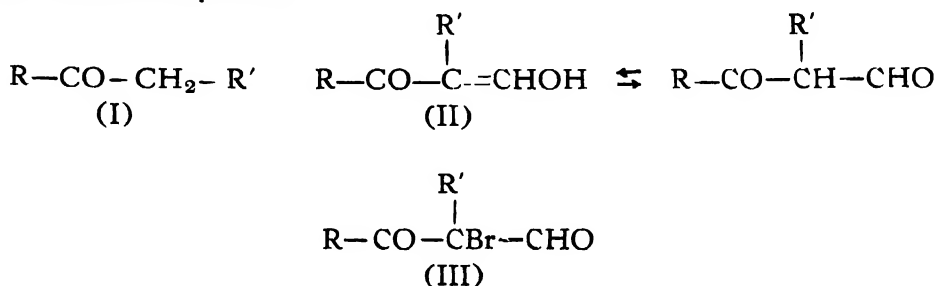
The above imino-ether hydrochloride (10g.) was finely powdered and treated with 15% alcoholic ammonia (100 c.c.) and the mixture was heated in a closed vessel at 65° to 70° for 5 hours. After cooling overnight, the almost colorless precipitate was filtered, washed with alcohol and dried in a vacuum desiccator. It was treated with cold, dilute hydrochloric acid and the solution was filtered to remove a minute quantity of suspended impurity and then basified with ammonia. On scratching, the solution gradually yielded a solid which was filtered and washed with cold water till free from any chloride, yield 2.5g. It was crystallised from hot water in colorless plates, which were dried *in vacuo* over fused calcium chloride. It melts to a viscous liquid at 310°. (Found : N, 12.01 ; As, 32.27.  $C_7H_9O_2N_2As$  requires N, 12.28 ; As, 32.86 per cent). It is readily soluble in cold, dilute hydrochloric acid and in cold dilute alkali but insoluble in aqueous ammonia or sodium bicarbonate. The *hydrochloride* was obtained as a colorless, crystalline powder by dissolving the compound in requisite quantity of dilute hydrochloric acid and pouring the solution into a large excess of acetone. It does not melt even at 325° and is fairly soluble in cold water.

# BROMINATION OF OXYMETHYLENE METHYL ETHYL KETONE AND OF OXYMETHYLENE ACETOPHENONE

By R. R. AGARWAL, S. M. GUPTA AND S. S. DESHAPANDE

Oxymethylene methyl ethyl ketone and oxymethylene acetophenone have been brominated in free condition and in the form of sodium compound respectively.

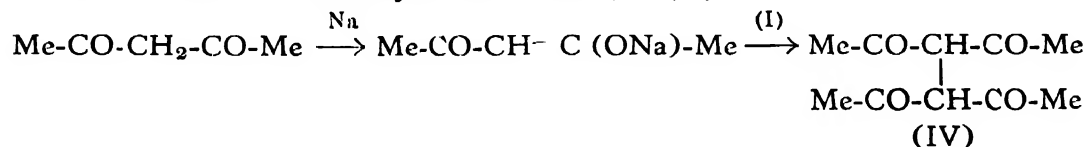
Bromination of oxymethylene ketones (formyl ketones) (II) derived from ketones (I) has been attempted only in few cases. It is carried out by adding bromine to the oxymethylene ketone, neutralised with caustic soda. Bromo-oxymethylene camphor and bromo-oxymethylene menthone are formed in this way (cf. Bruhl, *Ber.*, 1904, **37**, 2175, 2176). The structure (III) has been ascribed to these bromo compounds.



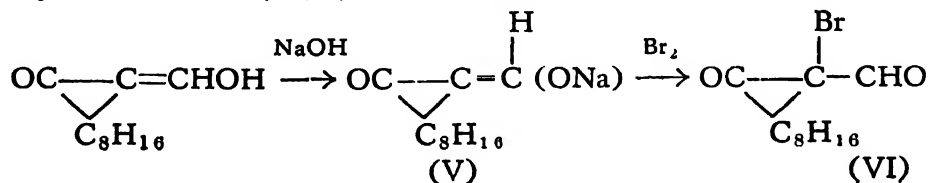
Bromination of oxymethylene *cyclohexanone* was, on the other hand, effected with the unneutralised ketone in ether solution by Mehta, Kaushal and Deshapande (*J. Indian Chem. Soc.*, 1946, **23**, 43) and the bromination product was obtained as an unstable solid, melting at 88-90°.

The bromination of oxymethylene methyl ethyl ketone (II, R=R'=Me) has been carried out in unneutralised condition and a bromo derivative (III, R=R'=Me) has been obtained as a fairly stable solid melting at 143°.

Keto-enolic systems  $\text{—CO—CH—CO—X}$  seem to differ from aldo-enolic systems  $\text{—CO—CH—CO—H}$  when the behaviour of their sodium compounds with halogens is considered. Thus, whereas sodium acetylacetone reacts with iodine (1 atom) to form 3 : 4-diacetylhexane-dione (2 : 5) (IV)



sodium oxymethylene menthone (V) gives with bromine (2 atoms) bromo-oxymethylene menthone (VI) (Bruhl, *loc. cit.*).



We have found that oxymethylene acetophenone (II,  $R = Ph$ ;  $R' = H$ ) behaves exactly similarly. Its bromination has been effected by suspending its sodium compound in ether and adding to it bromine (2 atoms). The bromo compound (III,  $R = Ph$ ;  $R' = H$ ) is a remarkably stable solid melting at  $106^\circ$ . Direct bromination of oxymethylene acetophenone is difficult as the free ketone readily undergoes self-condensation to 1:3:5-tribenzoylbenzene (Claisen and Stylos, *Ber.*, 1888, 21, 1145).

#### EXPERIMENTAL

*Bromo-oxymethylene Methyl Ethyl Ketone*.—Oxymethylene methyl ethyl ketone (7g), prepared from methyl ethyl ketone, alcohol-free sodium ethylate and ethyl formate, was dissolved in dry ether and the solution cooled by ice. Bromine (2 atoms), suspended in dry ether, was gradually added keeping the temperature at  $0^\circ$ . A white solid began to separate. In one experiment it was observed that if more than two atoms of bromine were added the solid which first separated again dissolved and on removal of the solvent a brown syrup was left which evolved hydrobromic acid. When exactly two atoms of bromine were added, a white solid was formed which was filtered at the pump and repeatedly washed with small amounts of dry ether, yield 7g. It could not be crystallised. It melts at  $143^\circ$ . (Found: Br, 44.1.  $C_7H_7O_2Br$  requires Br, 44 per cent). The bromo-oxymethylene ketone reduces Fehling's solution on warming.

*Bromo-oxymethylene Acetophenone*.—The sodium compound of oxymethylene acetophenone was formed when acetophenone, condensed with ethyl formate in presence of sodium in ether, was filtered at the pump and washed with dry ether. The sodium compound was suspended in carbon tetrachloride and bromine (2 atoms), dissolved in the same solvent, was added gradually to the suspension kept at  $0^\circ$ . The sodium bromide was filtered off and from the filtrate the solvent was removed. A thick syrup was left which immediately solidified. Crystallised from acetic acid the bromo compound melts at  $106^\circ$ . (Found: Br, 35.5.  $C_9H_7O_2Br$  requires Br, 35.2 per cent). The bromo-oxymethylene ketone gives acid reactions due to the persistence of aldo-enolic system in it. It dissolves in dilute alkaline solutions from which it is reprecipitated by acids.



## ON THE BASE EXCHANGE POWER OF CLAY MINERALS\*

By S. N. BAGCHI

The most important and characteristic property of clays is their base exchange capacity (b.e.c.). As the clay minerals are the dominant constituents of clays, their base exchange capacity is rightly attributed to these clay minerals.

Four groups of clay minerals have been distinguished. These are (1) the kaoline group having the chemical composition  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ; (2) the montmorillonite group derived from the ideal formula  $(\text{Al}_2)(\text{Si}_4)\text{O}_{10}(\text{OH})_2$  of pyrophyllite; (3) the illite group or the hydrous micas differentiated from muscovite mica,  $\text{K}(\text{Al}_2)(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$ , by their relatively small content of potassium and large percentage of water, and (4) the attapulgite group having the composition  $(\text{OH}_2)_1(\text{OH})_2\text{Mg}_5\text{Si}_8\text{O}_{20} \cdot 4\text{H}_2\text{O}$ .

The table below gives the values of b. e. c. 's of these clay minerals as compiled by Grim (*J. Geol.*, 1942, 50, 225).

TABLE I

B. e. c. (m. e.) per 100 g

Kaolinite	3-15	Attapulgite	25-30
Montmorillonite	60-100	Illite	20-40

All of these minerals, however, possess the same general scheme of atomic structure (cf. Pauling, *Proc. Nat. Acad. Sci. U. S. A.*, 1930, 16, 123). This consists of fused sheets of tetrahedral silica and octahedral hydrargillite (or brucite). Kaolinite is built up of unsymmetrical packets consisting of one sheet of tetrahedral silica fused to a sheet of octahedral hydrargillite. In montmorillonite the two sides of the octahedral layer are attached to two tetrahedral layers. But  $\text{Al}^{+++}$  and  $\text{Si}^{++++}$ , which are the only cations (leaving aside  $\text{H}^+$  ions of OH groups) contained in these ideal structures, are not the usual exchangeable bases of clays. How do these exchangeable bases come in? Why the b.e.c. of montmorillonite differs so widely from that of kaolinite? A correct answer to the first question seems to satisfy the second one too.

Naturally occurring montmorillonites contain a large amount of cations other than  $\text{Al}^{+++}$  and  $\text{Si}^{++++}$ . Kaolinite, however, is practically free from them.

\* Submitted at a symposium on base exchange of clays, held at Delhi Session of Indian Science Congress in January 1947.

has rightly been suggested that during the growth of the crystals isomorphous replacements within the lattice takes place and in order to balance the charge excess cations are held within the lattice (Hendricks, *J. Geol.*, 1942, 50, 276).

From dimensional considerations it appears very probable that the unsymmetrical structure of kaolinite would not be able to bear the strain of incorporation of cations other than  $\text{Si}^{++++}$  and  $\text{Al}^{+++}$  within the lattice (cf. Pauling, *Proc. Nat. Acad. Sci. U. S. A.*, 1930, 16, 578). Actually we find almost a complete lack of isomorphous replacement in these minerals. And consequently there could be no mono- or bivalent cations like those encountered in montmorillonites.

The work of Marshall (*Trans. Faraday Soc.*, 1930, 26, 173 ; *Z. Krist.*, 1935, 91, 431), Nagelschmidt (*Min. Mag.*, 1938, 25, 140), Hendricks *et al.*, (*J. Amer. Chem. Soc.*, 1940, 62, 1457 ; *Soil. Sci.*, 1943, 56, 285) and Giesking (*Soil Sci.*, 1939, 47, 1) have definitely shown that exchangeable bases are the integral constituents of the lattice. Moreover, in montmorillonites they are just those cations which have been incorporated into the lattice as a result of these isomorphous replacements. A more direct evidence of this hypothesis, viz., that the 'excess cations' are the usual exchangeable bases, is furnished by feldspars and zeolites whose atomic structures are more thoroughly known.

But kaolinite, as has already been pointed out, contains practically no mono- or bivalent cations. To what is then its b.e.c. due ? Opinion in this case differs. Hendricks (*Ind. Eng. Chem.*, 1945, 37, 625) recently suggested that the base exchange power of kaolinitic minerals is due to the unsatisfied valencies developed as a result of lattice termination. The cations are fixed up by the negative ends of the broken bonds of these ionic lattices. It is to be noted that in order to satisfy 'microscopic neutrality' of the individual crystallites, whenever a negative end arises simultaneously there appears a positive end which ought to take up anions. This amphoteric character of broken bonds has recently been stressed by Mitra (*J. Indian Chem. Soc.*, 1946, 23, 386). But if the broken bonds are responsible for the base exchange power of kaolinite, it is expected that they should also play their part in the case of other ionic lattices. The accumulated evidences on montmorillonites, feldspar and zeolites, however, show, as has already been pointed out, that it is the 'excess cations' of the lattice, and not those fixed by broken bonds (if fixed at all), which are responsible for their base exchange power.

It is more probable that  $\text{H}^+$  ions of OH groups of kaolinite lattice are responsible for its b.e.c., as has been suggested by Kelley and his co-workers (*Soil Sci.*, 1936, 41, 367). On this basis a plausible explanation is found for the dibasic acid character of hydrogen kaolinite as observed by Mukherjee and co-workers (*Ind. J. Agric. Sci.*, 1942, 12, 889). In kaolinite which has a polar structure, two crystallographically different types of OH groups exist. The exposed OH groups are expected to be more basic and show a greater resemblance with those of pure  $\text{Al}(\text{OH})_3$  than the subsurface OH groups

whose greater acid character can be traced to their location in a more acidic environment arising from a bonding of the basic alumina to acidic silica. The two types of OH groups will have different bonding energies and different degrees of dissociation. Hydrogen ions in two affinity levels are thus expected and these would be responsible for the observed dibasic acid character.

The question naturally arises what part the OH groups of montmorillonite lattice play in the b.e.c. of this mineral? Why hydrogen montmorillonites show monobasic acid character? The b.e.c. due to OH group alone (if we accept the measure of kaolinite) is a small fraction (about 10%) of that of montmorillonite. That the OH groups of montmorillonite lattice can play their part appears from the fact that its ideal structure, pyrophyllite, which contains no mono- or bivalent cation, also possesses a definite but small b.e.c. comparable to kaolinite (Kelley *et al.*, *loc cit.*). Hence, their contribution, if there be any, is perhaps overlooked. The b.e.c. of hydrogen montmorillonite is due mainly to the  $H^+$  ions on the surface of the packets derived from an exchange of the balancing cations of the lattice. Being at a considerable distance from the centres of negative charges, these  $H^+$  ions are expected to be more dissociable than the  $H^+$  ions of the OH groups. Further, the first stage of dissociation involving the former category of  $H^+$  ions will tend to suppress that of the hydroxylic hydrogens as in the case of polybasic acids. The observed monobasic acid character of hydrogen montmorillonite is therefore expected being due to a neutralisation of these readily dissociable  $H^+$  ions. A second inflexion in the titration curve due to hydroxylic hydrogens, though not incompatible with structural considerations, is not observed, being too weak for detection as in the case of the third stage of dissociation of phosphoric acid (c.f. Britton, "Hydrogen Ions").

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## A NOTE ON THE LIMITS OF SUPERSATURATION AND THE PARTICLE SIZE OF THE SOLUTE

By B. S. SRIKANTAN

Miers (*J. Inst. Metals*, 1927, 37, 331) postulates the existence of a definite supersolubility curve on the high concentration side of the normal solubility curve. For concentrations between the solubility curve (AB) and the supersolubility curve (CD), the equilibrium is meta-stable and supersaturation can exist there, as long as the solution is not seeded. On the high concentration side of the curve CD, the region has been termed labile, and solutions in the region G will spontaneously crystallise until the concentration of the solution falls to that demanded by the normal solubility curve AB. This proposal, though attractive, leaves undecided the question of how definite is the region between the supersaturated and the labile regions and the factors affecting the boundary of the meta-stable region. His experiments led him to conclude that spontaneous crystallisation occurred at a definite temperature on cooling a solution but not above this temperature. However, he cites examples of supercooling without crystallisation. Again, the high supersaturation exhibited by substances like sodium thiosulphate, copper sulphate and others as against sodium chloride etc., are to be explained. It is to be noted that his observations are on thermodynamically unstable systems which lie between the two stable states viz. (i) the saturated solution in equilibrium with the extra solute, and (ii) the state after relieving of the supersaturation by spontaneous crystallisation on undercooling. Unless the steps involved in this transfer are definitely known, it is not possible to establish the limits of supersaturation with any degree of certainty (cf. Ostwald, *Z. physikal. Chem.*, 1897, 22, 306).

Under conditions of stable equilibrium it has been shown by the author (this *Journal*, 1945, 22, 55) that supersolubility is controlled by the size of the particles with which that solution is in contact. Thus

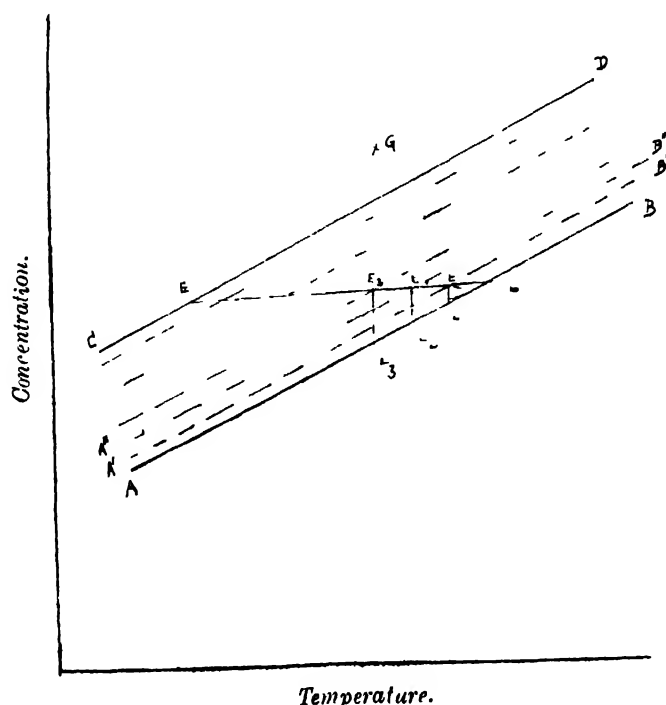
$$r(S - S_n)/S_n = K,$$

where the terms have the usual significance as before. From this it is at once evident that a solution may be supersaturated for particles of a certain size and at the same time unsaturated for particles of smaller dimensions at constant temperature. It becomes therefore obvious that with different particle sizes various solubility curves could be obtained similar to the normal solubility curve *i.e.*, with macro sizes.  $r = \infty$  has been shown to have a maximum limiting value of  $5.0\mu$ . Thus A'B', A'B'', ... are the solubility curves with different particle sizes  $r_1, r_2, \dots$ . There is, however, a limit for this series of curves, defined by the equation  $S/S_n = e^{K/r}$ . This equation has been shown by the author (*ibid.*, 1948, 25, 57) to be valid for all

values of  $k/r < 1$ . As it approaches unity, the value of  $r$  verges on the dimensions of colloidal particles and in that region there is no longer the heterogeneous equilibrium of solid-saturated solution but is entirely guided by other factors. So, the lower limit for the supersaturation region is defined by  $k=1$  or when the value of  $r$  is on the maximum side of the dimensions of colloidal range. Hence, the supersolubility region is bounded by the values of  $r=5.0\mu$  and  $r=50\mu$ . Thus under conditions of equilibrium of saturation, solutions with definite particle sizes of the solute, the meta-stable region becomes one of supersaturation equilibria with different particle sizes of the solute and the region beyond is one of colloids with entirely different properties not controlled by conditions of thermodynamic equilibria.

*Conditions for Spontaneous Crystallisation on Supercooling.*—Considering a point L on the normal solubility curve AB, the saturated solution is in equilibrium with the solute particles of radius  $r=\infty$ . If assuming that in the process of supersolution at L all the particles are equally affected and the change in  $r$  goes through  $r_1, r_2, r_3, \dots$  where  $r_1 > r_2 > r_3 > \dots$ , the effect of cooling adiabatically from  $T_s$ , the temperature of saturation, leads to important conclusions. The temperature line parallel to the X-axis cuts the supersaturation curves at points  $E_1, E_2, E_3, \dots$ . The point  $E_1$  on the A'B' line could be reached when  $r=r_1$ .  $E_1L_1$  is the excess solubility over normal solubility at  $T_1$ .

FIG. 1



To arrive at this state of supersaturation all particles from  $r=\infty$  change to  $r_1$ . Thus one can pass from L to E with change to smaller dimensioned

particles, supercooling maintaining supersolubility. But other factors are also operative. There is a tendency for crystallisation working in the opposite direction at each of the points  $E_1, E_2, \dots$ . This depends on the number of the nuclei present which are smaller than  $r$  at its various values. Thus, at  $E_1$ , where the size of the solute particle is  $r_1$ , the nucleus for growth should depend on the number of particles having sizes less than  $r_1$ . The formation of nuclei is a slow process, while their growth is fairly rapid when once formed. This is an ideal condition where all the particles are, to start with, of uniform size; but in practice the starting is not uniform with reference to the size of the particles, and further, according to equation cited above, the larger particles tend to grow and decrease the supersolubility, and the finer particles tend to dissolve and also act as nuclei for growth of crystals. The final result will depend on the chances of smaller particles dissolving or acting as nuclei for the spontaneous shower and growth of crystals. Thus, for substances like sodium thiosulphate, copper sulphate which show high solubility and also temperature coefficient of solubility, high supersolubility will be maintained on cooling, but for substances with low solubility and also those with low temperature coefficient of solubility like sodium chloride and barium chloride, the tendency for the spontaneous growth and crystallisation will be more evident than maintaining supersolubility on cooling.

Blythe, Martin and Tongue (*Nature*, 1923, 111, 842) derive in the case of mechanical subdivision the equation  $N = ab^{-br}$  or  $dN/dr = -bN$ , which shows that the rate of increase of the number of particles present of any given size with the decrease of diameter is proportional to the number ( $N$ ) of particles of that size. So, if one starts with particles of two sizes  $r_1$  and  $r_2$ ,  $r_2$  being smaller than  $r_1$ , the rate of increase of the number of particles of  $r_1$  is proportional to the number of particles of  $r_1$ . Hence, the number of  $r_1$ , if it is less than that of  $r_2$ , no shower of crystals will form or if  $r_1/r_2$  is great, there is a chance for spontaneous crystallisation and growth. If  $T_s$  is the temperature of saturation under ordinary conditions and  $T_c$  is the temperature of spontaneous crystallisation and growth,  $T_c - T_s$  will be small if  $r_1/r_2$  is great and *vice versa*.



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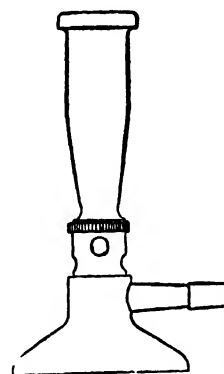
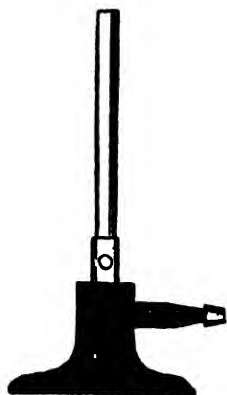
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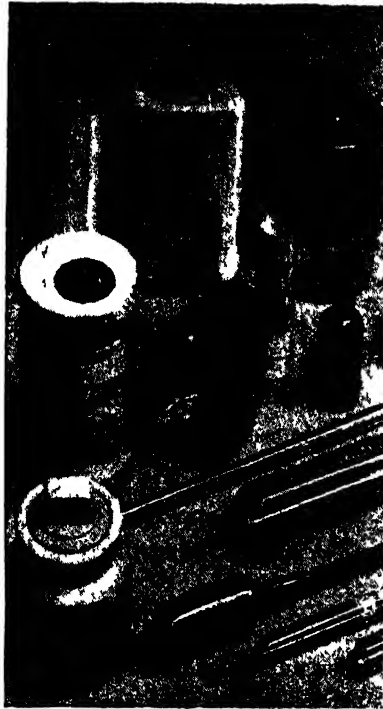
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## SYSTEM $[\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}]$ IN RELATION TO THE DEHYDRATING PROPERTIES OF ALUMINA

By A. JAYARAMAN AND B. S. SRIKANTAN

The isobars of alumina, prepared from different sources have been obtained and their mechanism of water holding has been discussed in relation to their different catalytic activity. The catalytic activity is dependent on the capacity of alumina to hold water in 'zeolitic condition'. Tendency to form hydrates is shown alumina, which is known to be a poor catalyst.

Adkins and his co-workers (*J. Amer. Chem. Soc.*, 1922, **44**, 385, 2175 ; 1923, **45**, 809 ; 1924, **46**, 130, 2291 ; 1925, **47**, 807) found that alumina prepared in different ways exhibited varying catalytic activity towards the decomposition of formic acid, alcohols, and esters. This could be hardly ascribed to the different surface areas of the several preparations, as the variation was not confined to the total speed of the reaction but also affected the relative speeds of two alternate modes of decomposition which these substances undergo e.g., (i) dehydration and (ii) dehydrogenation in the case of alcohols and formic acid. They stress on the difference in the spacing of the aluminium atoms rather than the ability of alumina to absorb water during dehydration, as a plausible explanation for the difference in activity. X-ray and electron diffraction studies on aluminium hydroxide and alumina (*vide infra*) do not confirm the difference in spacing of the aluminium atom in the various preparations. Further, the experimental results of Adkins and Nissen (*loc.cit.*) on the formation of nitriles from amides stand in sharp contrast to their own suggestion. However, a study of alumina-water system might afford a clue to the nature of alumina as a dehydration catalyst, since according to Dover and Marden (*J. Amer. Chem. Soc.*, 1917, **39**, 1609) the loss of water on heating  $\text{Al}(\text{OH})_3$  up to  $500^\circ$  is quantitatively reabsorbed if the ignited sample is kept in moist air for 24 hours.

Weiser and Milligan (*J. Phys. Chem.*, 1934, **38**, 1175 ; 1940, **44**, 1081) from X-ray and electron diffraction studies conclude that all precipitated varieties of hydrous oxides of alumina are as  $[\gamma\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}]$  which transform through the unstable  $[\alpha\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}]$  to the stable  $(\gamma\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O})$ . Starting from different materials they find that the same structure is obtained though the size of the primary crystals may vary as in the case of aluminium hydroxide from sulphate.

Fricke and Severin (*Z. anorg. Chem.*, 1932, **205**, 287) report X-ray evidence for  $[\gamma\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}]$  in the sample of aluminium hydroxide by precipitation by  $\text{CO}_2$  on sodium aluminate. Weiser and Milligan (*loc.cit.*) report that  $[\alpha\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}]$  changes into  $[\gamma\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}]$  at  $205^\circ$ , though stable up to  $145^\circ$ . The hydroxide from sodium aluminate is stable up to  $160^\circ$  and decomposes by losing water thereafter at a slow and steady rate.

Mead (cf. Milligan) finds that while the hydroxide shows X-ray evidence for  $[\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}]$  but on igniting to  $325^\circ$  there is no trihydrate but only evidence of crystalline  $[\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}]$  and corundum structure of  $\text{Al}_2\text{O}_3$  and that absorption of water does not alter the structure. Isobaric studies of Milligan (*J. Phys. Chem.*, 1922, **26**, 247) give no support for a monohydrate, while Rooksby (*Trans. Ceram. Soc.*, 1929, **28**, 399) reports a monohydrate, and Edward and Tosterud (*J. Phys. Chem.*, 1933, **37**, 433) give evidence of a second monohydrate.

From the above, the nature of hydroxide formed is not definite except in certain main details and does not help us far in the problem of Adkin's catalysts. It is proposed in this paper to study in detail the isobars of aluminium hydroxide prepared by different methods with a view to elucidating the mechanism of their water holding, since according to Bancroft (*J. Phys. Chem.*, 1917, **21**, 602) a catalyst tends to produce that system which it absorbs most strongly.

## EXPERIMENTAL

### *Preparation of Aluminium Hydroxide*

(a) *From the Nitrate*.—Aluminium nitrate crystals (50 g. of C.P., Rideal de Haehn) was dissolved in 350 c.c. of distilled water and the solution was boiled for a few minutes. To this solution was added ammonia (sp. gr. 0.91) dropwise with stirring till the precipitation was complete. The precipitate was boiled with a large excess of water and kept boiling for 15 minutes. It was filtered and the precipitate washed till free from nitrate and ammonia. The precipitate was dried at 100° in an oven for 5 hours and ground to fine powder in an agate mortar, sieved to 100 mesh and kept in a vacuum desiccator over silica gel drier.

(b) *From Ammonium Alum*.—Ammonium alum (B.D.H. Analar, 112.5 g.) was dissolved in 500 c. c. of distilled water and the solution boiled. Ammonia (sp. gr. 0.91) was added dropwise with stirring till complete precipitation. The hydroxide was boiled with a large quantity of water for 15 minutes, filtered and washed free from ammonium sulphate. The precipitate was dried at 95° for 5 hours. The sample was ground in an agate mortar, sieved to 100 mesh and stored as above in a desiccator.

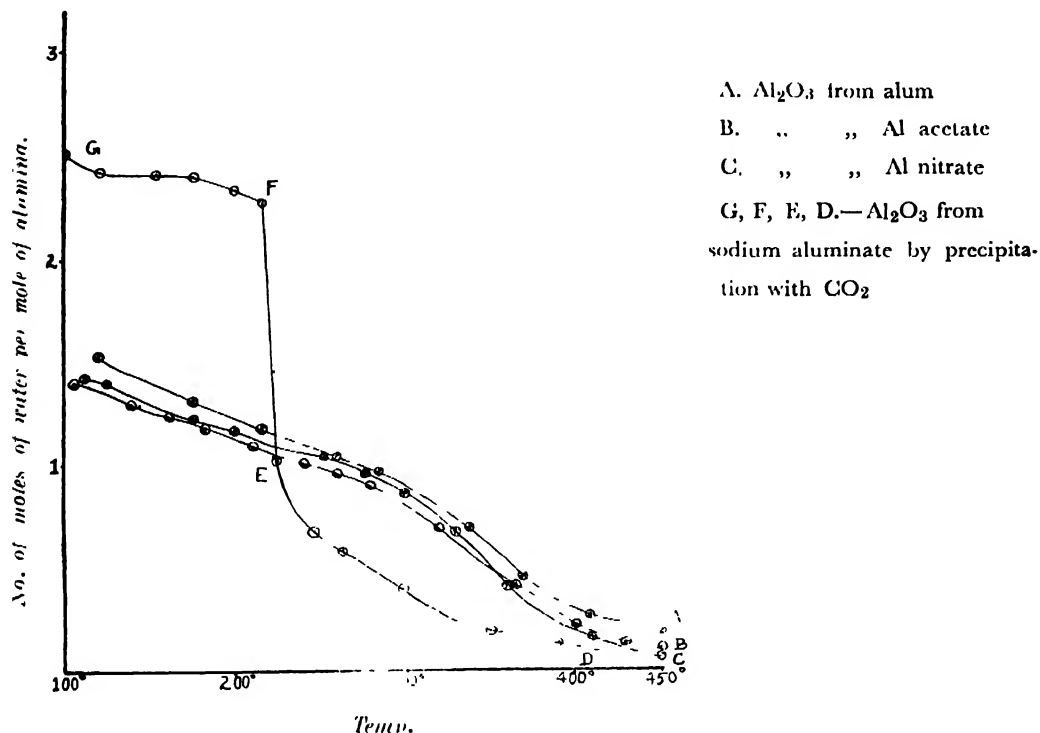
(c) *From Aluminium Acetate*.—Pure aluminium acetate (Johnson, 20 g.) was taken in 500 c.c. of distilled water and hydrolysed under repeated boiling. The insoluble basic salt was filtered, washed free from acetic acid, and the precipitate was treated with a few c. c. of ammonium hydroxide and boiled with additional water. This was repeated twice over and the complete hydrolysis was over in 3 days. The sample was thoroughly washed till free from acetic acid and ammonia, dried at 90° for 8 hours, ground, sieved to 100 mesh and stored as above.

(d) *Le Chatelier Method*. The aluminium hydroxide from (b) above, was dissolved in sodium hydroxide (6*N*) and filtered. The solution was maintained between 60° and 70° and a slow and steady stream of CO<sub>2</sub> was passed into it. The precipitated alumina was filtered, washed free from traces of caustic soda and carbonate, dried at 100° and sieved to 100 mesh. The sample was kept in the desiccator as above.

*Isobars of Aluminium Hydroxide Samples*.—Alumina (1 to 2 g.) was weighed accurately and kept in a calibrated electric furnace, temperatures of which were maintained at different values from 100° to 400° in steps of 10°. The temperature in each case was kept constant within ±2°. The samples were kept at each temperature for 3 hours and more and weighed to constant weight after cooling in a desiccator. Final heating at 400° dehydrated the samples completely. Several experiments were conducted with each

type of alumina described above and concordant results obtained. On the initial and the final weights of the samples, the number of moles of water held by per mole of alumina was calculated. The graphs in Fig. 1 give the representative value for the isobars of alumina prepared from different starting materials and by different methods. The initial water contents were below 3 moles of water per mole of alumina since observations were made only on samples heated to  $100^\circ$  below which some quantity of water might have been lost.

FIG. 1



## DISCUSSION

It is seen from the results presented in Fig. 1 that the nature of the Le Chatelier's alumina is entirely different from those of the others obtained by precipitation from the different salts of aluminium. The latter give similar isobars and form a class by themselves. The curves (A, B & C) for the system,  $[\text{Al}_2\text{O}_3\text{--H}_2\text{O}]$  is bivariant and give continuous desorption curves. The curves for hydrates according to phase rule are univariant giving stepped curves denoting a definite hydrate at each step. There appears to be no definite monohydrate in these cases and the stoichiometric formulae describe only a limiting composition. Water is removed by dehydration in a continuous manner without giving rise to a new solid phase. Emeleus and Anderson ("Modern Aspects of Inorganic Chemistry", 1942, p. 163) consider from similar cases that water is neither bound by covalent bonds nor hydrogen bonds as in the case of regular hydrates but as being packed between the layers of the crystal or in the interstices of the structure. Water held in such a manner is classified by them as 'zeolite water.' The removal of zeolite water according to them

may change the spacing between the successive layers of the crystal. The curve (G,F,E,D) for the same system is made up of two bivariant systems (GF & ED), one with a limiting composition of 3 moles of water and the other of 1 mole of water. Thus, the sudden transition (FE) at  $220^{\circ}$  denotes a change from one bivariant system to another. This part of the curve is similar to that which would be obtained in a univariant system [ $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ ,  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ - $\text{H}_2\text{O}$  vapour]. In this case water above 1 mole according to Emelius and Anderson (*loc. cit.*) would be what is described as "lattice water", which is a border case between chemically bound water and "zeolite water".

From Adkin's work (*loc. cit.*) it is seen that precipitated alumina from aluminium salts is about 1.5 times more active than that prepared by Le Chatelier method for dehydration. So it could be concluded that capacity of alumina to hold water in zeolitic condition gives a more active variety of catalyst for dehydration reactions than either lattice type or chemically bound type of water holding : Removal of zeolitic water, altering the spacing of the successive layers of the crystal, might help to render the catalyst more active. Evidence for this view is forthcoming in the recent work of Bentley and Faechim (*J. Soc. Chem. Ind.*, 1945, **64**, 148) who rendered a relatively less active alumina into an active dehydration catalyst by alternate hydration and dehydration. Thus the difference in the activity of alumina catalyst in dehydration processes would appear to be due to the difference in the mode of water of holding and not to the spacing of the aluminium atoms.

It is well known that fineness of subdivision increases the catalytic activity. In the case of alumina, such subdivision might increase the area of the effective surface or might alter the mechanism of water holding. Experiments of Hagiwara (J. Alexander, "Colloid Chemistry", 1926, Vol. I, pp. 647-658) on the isobars of aluminium hydroxide show that fine grinding changes the curve from univariant one to a bivariant one. In other words, fine particles take up water in a zeolitic manner, while bigger crystals form definite hydrates.

The authors' thanks are due to Principal Dr. J. J. Rudra, M.B.E., for his kind interest.

## VARIATION OF ABSOLUTE VISCOSITY WITH CONCENTRATION.

## ORGANIC SOLUTES IN NON-AQUEOUS SOLVENTS

By A. N. BOSE

The viscosity of non-electrolytes in non-aqueous solvents has been studied at different concentrations. It has been found that Tainini's second equation  $\log \eta = \theta_c + \phi$  is applicable to the most of the systems studied here. The values of the constants,  $\theta$  and  $\phi$ , of the above equation have been calculated.

In a previous communication by Bose (this *Journal*, 1948, **25**, 33) the variation of viscosity with concentration has been studied. In the present paper the same work has been extended to the other systems of organic solutes in non-aqueous solvents.

The experimental method employed for the determination of viscosity is the same as in the previous paper. Results obtained are given in Table I.

The viscosity was determined at four different concentrations and at various temperatures. The observations at only two different temperatures, lowest and the highest, are recorded below. The concentrations given are expressed in grams of anhydrous solute in 100 grams of pure solvent.

TABLE I

Solute.	Temp.	Viscosity at different concentrations.			
		Solvent = MeOH.			
		$c =$ 68.0	74.0	83.0	93.0
Benzoic acid	30°	0.011960	0.012900	0.013600	—
	45°	0.009466	0.010020	0.010530	0.011330
Salicylic acid		$c =$ 65.0	72.0	75.0	88.0
	35°	0.010490	0.010860	0.011180	0.012620
	50°	0.008273	0.008572	0.008818	0.009692
Phthalic acid		$c =$ 24.6	29.5	33.0	37.0
	35°	0.009160	0.010010	0.01085	0.011680
	50°	0.007180	0.007900	0.008526	0.009060
Cinnamic acid		$c =$ 37.5	42.4	45.0	50.3
	35°	0.008921	0.009758	0.010140	0.010920
	50°	0.007246	0.007679	0.007970	0.008460
<i>m</i> -Nitro benzoic acid		$c =$ 110.7	144.40	156.6	167.0
	35°	0.018850	0.024850	0.027730	0.030250
	50°	0.014210	0.018030	0.020260	0.021620
Succinic acid		$c =$ 19.6	25.5	27.8	33.5
		0.008055 0.006460	0.009203 0.007331	0.009556 0.007603	— 0.008441

TABLE I (*contd.*)

Solute.	Temp.	Viscosity at different concentrations.				
		Solvent = Propyl alcohol.				
Benzoic acid		$c =$	40.0	44.0	50.0	56.0
	30°		0.025310	0.026030	0.027240	0.028440
	45°		0.017700	0.018160	0.018810	0.019650
Salicylic acid		$c =$	35.4	43.7	50.0	54.3
	35°		0.021300	0.022360	0.024270	0.024000
	50°		0.015100	0.016020	0.016900	0.017220
Phthalic acid		$c =$	5.6	7.8	10.6	13.5
	40°		0.0163200	0.017320	0.018870	—
	55°		0.012650	0.012390	0.013310	0.014240
Cinnamic acid		$c =$	18.2	24.1	30.3	34.2
	35°		0.020660	0.022240	0.024400	—
	55°		0.012900	0.014000	0.015060	0.015870
<i>m</i> -Nitrobenzoic acid		—	78.4	89.7	98.3	108.0
	45°		0.030070	0.032860	0.036200	0.039510
	55°		0.023240	0.025200	0.027810	0.030180
Succinic acid		$c =$	6.1	7.5	8.8	9.8
	40°		0.016570	0.017200	0.017770	0.018880
	55°		0.011900	0.012140	0.012710	0.013130
Solvent = Butyl alcohol.						
Salicylic acid		$c =$	30.3	39.0	44.5	50.5
	35°		0.024530	0.026560	0.027610	—
	55°		0.015500	0.016730	0.017250	0.017940
Phthalic acid		$c =$	4.9	7.3	9.2	—
	45°		0.018060	0.019280	0.019850	—
	50°		0.016040	0.017120	0.017800	—
Cinnamic acid		$c =$	15.7	21.2	25.6	—
	45°		0.019320	0.020730	0.021800	—
	55°		0.015320	0.016380	0.017210	—
Succinic acid		$c =$	2.7	5.8	7.8	—
	45°		0.017040	0.018480	0.019430	—
	55°		0.013570	0.014730	0.015410	—
Solvent = Acetone.						
Benzoic acid		$c =$	56.9	53.0	62.5	69.1
	35°		0.006741	0.006647	0.007283	0.007500
	45°		0.005924	0.005884	0.006407	0.006571
Solvent = Nitrobenzene.						
Benzoic acid		$c =$	12.0	16.0	21.0	—
	40°		0.016260	0.016750	0.017460	—
	55°		0.013020	0.013330	0.013930	—

## DISCUSSION

From the results given in Table I, the following types of curves have been plotted: (a) viscosity against concentration, (b) log viscosity against concentration. Of these two types of curves, log viscosity against concentration is found to be more applicable to these systems also. The results for the plot of log viscosity against concentration is given in Table II. The plotted curves have been divided into three categories, viz., (i) those which give a straight line, (ii) those giving a positive curvature and (iii) those which give negative curvature.

TABLE II

Straight line.		Positive curvature.	Negative curvature.
1.	MeOH— Succinic acid	1. PrOH— Succinic acid	1. Acetone— Benzoic acid
2.	„ — Benzoic acid	2. Nitrobenzene— Benzoic acid	
3.	„ — Salicylic acid		
4.	„ — Phthalic acid		
5.	„ — Cinnamic acid		
6.	„ — <i>m</i> -Nitrobenzoic acid		
7.	PrOH — Benzoic acid		
8.	„ — Salicylic acid		
9.	„ — Phthalic acid		
10.	„ — Cinnamic acid		
11.	„ — <i>m</i> -Nitrobenzoic acid		
12.	BuOH — Salicylic acid		
13.	„ — Cinnamic acid		

From the results given above it is observed that the second equation of Taimina,  $\log \eta = \theta c + \phi$  ... (I) is obeyed by most of the systems studied here.

The values of  $\theta$  and  $\phi$  of the above equation (I) have been calculated for the system studied here. The results for  $\theta$  and  $\phi$  are given in Table III.

TABLE III

Temp. —45°.

Solute.	$\theta \times 10^{-3}$ .	$\phi$ .	$\eta$ of (calc.)	$\eta$ of pure solvent.
		Solvent MeOH.		
Benzoic acid	4.100	.6974	0.004982	0.004300
Salicylic acid	2.910	.7619	0.005780	
Phthalic acid	9.451	.6577	0.004546	
Cinnamic acid	5.146	.7022	0.005037	
<i>m</i> -Nitrobenzoic acid	3.428	.8198	0.006604	
Succinic acid	8.352	.6802	0.004790	

TABLE II—(contd.)

		$\theta \times 10^{-3}$ .	$\phi$ .	$\eta$ (calc.).	$\eta$ of pure solvent.
Solvent = Pr.OH.					
Benzoic acid	..	2.770	.1371	0.013710	0.012600
Salicylic acid	..	3.227	.1105	0.012900	
Phthalic acid	..	11.900	.0979	0.012530	
Cinnamic acid	..	5.322	.1149	0.013030	
<i>m</i> -Nitrobenzoic acid	..	4.441	.1167	0.013090	
Succinic acid	..	10.370	.1076	0.012810	
Solvent = BuOH.					
Salicylic acid	..	3.300	.1905	0.015510	0.01590
Phthalic acid	..	11.940	.1975	0.015760	
Cinnamic acid	..	5.543	.1990	0.015850	
Succinic acid	..	28.500	.0650	0.011610	
Solvent = Acetone					
Benzoic acid	..	3.573	.5823	0.003820	
Solvent = Nitrobenzene					
Benzoic acid	..	3.250	.1379	0.013790	

From the results given in Table III the following observations may be made :

(1) For the solutions of propyl alcohol—phthalic acid, propyl alcohol—succinic acid and butyl alcohol—phthalic acid the difference between the values of viscosity calculated and the viscosity of the pure solvent is within 1%.

(2) For the solutions of propyl alcohol—salicylic acid, propyl alcohol—cinnamic acid, propyl alcohol—*m*-nitrobenzoic acid, butyl alcohol—salicylic acid and methyl alcohol—phthalic acid the difference is within 5%.

(3) For the solutions of methyl alcohol—succinic acid and propyl alcohol—benzoic acid the difference is within 5% to 10%.

(4) For the rest of the solutions studied in this paper the difference is above 10%.

It is observed that for the systems of propyl alcohol and butyl alcohol, the difference between the value of the viscosity calculated from Taimini's equation and the viscosity of the pure solvent is not much as compared to the systems of methyl alcohol. This may be due to the solvation being more marked in the systems of methyl alcohol than those in propyl alcohol and butyl alcohol.

The author wishes to express his sincere thanks to Dr. A. C. Chatterji for his valuable suggestions and guidance in this work and to the U.P. Government for the grant of a research fellowship.



## SYNTHESIS OF SUBSTITUTED DINITROPHENYLKETONES AND PHENYLACETIC ACIDS. PART VI

By A. B. SEN AND P. M. BHARGAVA

2:6-Dinitro-4-iodophenyl-acetone and -acetic acid and 2-methyl-3-carbethoxy-5-amino-7-iodoindole have been prepared.

In the previous communications (Sen and Bhargava, this *Journal*, 1947, **24**, 268, 371, 403; 1948, **25**, 282, 538) the preparation of a number of halogenated dinitrophenylketones and phenylacetic acids has been described; the method employed was to condense a halogenated dinitrobenzene containing a reactive chlorine atom, with acetoacetic and malonic esters, and to submit the resulting product to hydrolysis. In this paper, this reaction has been extended to the preparation of 2:6-dinitro-4-iodophenyl-acetone and -acetic acid. The ketone has been characterised by the preparation of its phenylhydrazone; its oxime, however, could not be obtained. The reduction of 2:6-dinitro-4-iodophenylacetoacetic ester by iron powder and water yields an indole derivative.

### EXPERIMENTAL

4-Iodo-2:6-dinitrophenol was obtained previously by Armstrong (*Ber.*, 1873, **6**, 650) by the iodination of 2:6-dinitrophenol, but the exact experimental details being not available, it was prepared by us in the following way.

2:6-Dinitrophenol (20.5 g.) was dissolved in hot glacial acetic acid and a finely powdered mixture of iodine (30 g.) and freshly prepared yellow mercuric oxide (13 g.) was added to it gradually, during 1½ hours. Each addition was followed by heating the solution to boiling, and shaking till the colour of the iodine was discharged. After the addition was complete, the contents of the flask were stirred mechanically for one hour and then left overnight. The acetic acid layer was then decanted off and the residual mercuric iodide extracted twice, with 10 c.c. of glacial acetic acid each time. The combined acetic acid solutions were diluted with a small amount of water and the precipitate so obtained was filtered. On recrystallisation from hot alcohol, the iododinitrophenol was obtained as dark orange-red crystals, m.p. 112.5°. A further crop of the compound was obtained by concentrating the mother-liquor, yield 20 g. (58% of theory).

2:6-Dinitro-4-iodophenylacetoacetic Ester.—The sodium derivative of acetoacetic ester was prepared as usual, from acetoacetic ester (12.5 g.) and sodium (2 g.) in anhydrous benzene (75 c. c.). After the last traces of sodium had disappeared, the flask was cooled in ice and 1-chloro-4-iodo-2:6-dinitrobenzene (13 g.) (prepared from 4-iodo-2:6-dinitrophenol by the method of Sane and Joshi, *J. Indian Chem. Soc.*, 1932, **9**, 61) added. The contents of the flask were stirred mechanically for one hour in cold, then refluxed for 6 hours and left overnight. The mixture was then extracted with 2% caustic soda solution (300 c. c.), the extract cooled with ice and acidified with dilute nitric acid, when a red oil separated out. This was left to settle down in a refrigerator, when the greater part of the oil solidified. The supernatant liquid was then decanted off, the mixture shaken with 40 c. c. of cold alcohol and filtered. The dark reddish brown crystals

on the filter paper consisted of the dinitroiodophenylacetoacetic ester. Another crop of the ester was obtained by allowing the alcoholic filtrate to evaporate by itself, yield 14 g. (84% of theory). On recrystallisation by dissolving in hot alcohol, filtering and allowing the filtrate to evaporate slowly, the ester was obtained as very fine, pale yellow needles, m.p. 113-14°. (Found : N, 6.81.  $C_{12}H_{11}O_7N_2I$  requires N, 6.61 per cent).

*2:6-Dinitro-4-iodophenylacetone.*—The crude 2:6-dinitro-4-iodophenylacetoacetic ester (4 g.) was dissolved in sulphuric acid (concentrated, 45 c.c.), and to this, water (21 c.c.) was added slowly, with constant stirring and without cooling. The black solution was then allowed to stand for an hour, when the evolution of carbon dioxide ceased. It was then poured over crushed ice, allowed to stand in a refrigerator overnight and filtered, when the crude ketone was obtained as an almost black crystalline mass. On recrystallisation from hot alcohol, it was obtained as light brown crystals, m.p. 138-39°, yield theoretical. (Found : N, 8.12.  $C_9H_5O_2N_2I$  requires N, 8.0 per cent).

The *phenylhydrazone* of the above ketone was obtained by dissolving the crude ketone (1 g.) in hot alcohol (15 c. c.) and refluxing for one hour with phenylhydrazine (1.5 c.c.). The mixture was then cooled in ice, diluted with a small quantity of water and filtered. The dark coloured residue was dissolved in boiling alcohol, filtered hot and the filtrate allowed to evaporate slowly, when the phenylhydrazone separated out. On recrystallisation from a mixture of equal quantities of alcohol and acetone, the phenylhydrazone was obtained as a brown crystalline substance, m.p. 140-42° (decomp.), yield 0.5 g. (40% of theory). (Found : N, 12.38.  $C_{16}H_{13}O_4N_4I$  requires N, 12.73 per cent).

*2:6-Dinitro-4-iodophenylacetic Acid.*—The crude 2:6-dinitro-4-iodophenylacetoacetic ester (2 g.) was refluxed for one hour with 20% alcoholic potash (13 c.c.) to which one c. c. of water had been added. The alcohol was then distilled off, the residue cooled in ice and then acidified with hydrochloric acid. It was filtered and the dark coloured residue extracted with hot alcohol, the extract being filtered hot. The filtrate was allowed to evaporate by itself and the dark brown acid separating was purified by dissolving in sodium carbonate solution, filtering and reprecipitating with hydrochloric acid. It does not melt but gives off iodine on heating strongly, yield 1 g. (60% of theory). (Found : N, 7.66.  $C_8H_5O_6N_2I$  requires N, 7.95 per cent).

*2-Methyl-3-carbethoxy-5-amino-7-iodoindole.*—The crude 2:6-dinitro-4-iodophenylacetoacetic ester (1.5 g.), iron powder (2.5 g.), crystalline ferrous sulphate (0.25 g.) and water (8 c.c.) were refluxed for three hours. It was then cooled with shaking in ice and filtered. The residue was extracted four times, with 10 c.c. of alcohol each time, the extract filtered hot and the filtrate allowed to evaporate by itself when 2-methyl 3-carbethoxy-5-amino-7-iodoindole separated out as colorless crystals turning dark violet immediately on exposure to air, m.p. 194-95°, yield 1.1 g. (54% of theory). (Found : N, 7.91.  $C_{12}H_{13}O_2N_2I$  requires N, 8.14 per cent).

One of the authors (P.M.B.) is indebted to the Lucknow University for the award of a research grant for carrying out this work.

## CHARGE AND STABILITY OF COLLOIDS. PART XIV. EFFECT OF NON-ELECTROLYTES

By A. C. CHATTERJI AND RAM NATH

The effect of non-electrolytes such as propyl, isopropyl and butyl alcohol, glycol, glycerol and acetone on the stability of arsenious sulphide sol has been studied. It has been observed that the variations in the coagulation concentration of an electrolyte and the adsorption of oppositely charged ions of the same electrolyte do not always go hand in hand.

In part II of this series of papers (*J. Indian Chem. Soc.*, 1943, **20**, 109) the effect of non-electrolytes such as methyl alcohol, ethyl alcohol, agar agar and gelatin was studied. In this paper the work has been extended and the effect of propyl, isopropyl and butyl alcohol, glycol, glycerol and acetone has been studied from the viewpoint of the variation in the coagulation concentration and the adsorption of oppositely charged ions by the colloidal particles of arsenious sulphide sol.

It has been suggested in the previous paper (*loc. cit.*) that when protection takes place, the charge on the colloid need not necessarily increase appreciably. This view has been confirmed, and as a matter of fact, while stability against coagulation by electrolytes goes on increasing, the adsorption of oppositely charged ions near about the coagulation point instead of increasing actually decreases.

In this paper adsorption of oppositely charged ions by the colloidal particles of arsenious sulphide sol has been measured by the method given in part I of this series of papers (*J. Indian Chem. Soc.*, 1943, **20**, 25) in presence of various non-electrolytes, in varying concentrations, in order to find out how the adsorption varies under different conditions. Under the limitations, as pointed out in the same paper (*loc. cit.*), the charge on the colloidal particles has been calculated from the chemical adsorption alone, on the assumption that the adsorbed ions of the electrolyte displace all ions of the same sign in the electrical double layer.

### EXPERIMENTAL

The experimental procedure followed in this paper is the same as given in part I (*loc. cit.*). The coagulation concentrations for a particular sol of known concentration, when propyl and isopropyl alcohols were added in increasing amounts, are given in Table IA and IB respectively.

TABLE IA

Conc. of sol=20.1g./litre.  
Sol taken=5 c.c. Total volume=10 c.c.  
Time of coagulation=1 hour.

PrOH added (% by volume).	Coagulating conc. of N/80- BaCl <sub>2</sub> .
0 c.c.	1.9 c.c.
1	2.05
10	2.6
20	5.0
30	5.6

TABLE IB

Conc. of sol=21.94 g./litre.  
Sol taken=5 c.c. Total volume=10 c.c.  
Time of coagulation=1 hour.

isoPrOH added (% by volume).	Coagulating conc. of N/80- BaCl <sub>2</sub> .
0 c.c.	2.0 c.c.
1	2.05
10	2.2
15	2.3
20	2.5

From the above tables a stabilisation is observed with propyl alcohol and isopropyl alcohol towards electrolytes. In the following tables the adsorption of oppositely charged ions by the particles of arsenious sulphide sol, when non-electrolytes are added in varying concentrations, are given.

TABLE II

*Variation in the adsorption of Ba-ions by the particles of arsenious sulphide sol when propyl alcohol is added in increasing concentrations.*

Conc. of the sol=20.01 g./litre. Radius of the particle=75 $\mu\mu$ (by extra polation). Sol taken=200 c.c. Total volume=400 c.c. No. of particles in the sol taken=6.376  $\times 10^{14}$ .

Nature of sol.	N/20-BaCl <sub>2</sub> added.	Adsorption of Ba ions			Charge $e.n.H. \times 10^6$
		Total.	Physical.	Chemical.	
Sol + water	22 c.c.	.002645 g.	0.01265 g.	0.01380 g.	9.13
Sol + 1c.c. alcohol	22	.02710	.01268	.01442	9.54
" + 2 " "	23	.02690	.01270	.01420	9.39
" + 4 " "	23	.02657	.01268	.01389	9.19
" + 8 " "	25	.02610	.01266	.01344	8.89
" + 16 " "	25	.02487	.01268	.01219	8.06
" + 32 " "	26	.02410	.01268	.01142	7.55
" + 50 " "	30	.02308	.01260	.01048	6.93

TABLE III

*Variation in the absorption of Ba-ions by the particles of  $As_2S_3$  sol when isopropyl alcohol is added in increasing conc.*

Conc. of the sol=21.94 g./litre. Radius of the particles= $75 \mu\mu$  (by extrapolation).  
Sol taken=200 c.c. Total volume= 400 c.c. No. of particles in the sol taken= $6.99 \times 10^{14}$ .

Nature of sol.	N/20-BaCl <sub>2</sub> added.	Adsorption of Ba-ions			Charge e.s.u. $\times 10^6$ .
		Total.	Physical.	Chemical.	
Sol + water	22 c.c.	0.03130 g.	0.01540 g.	0.01590 g.	9.55
Sol + 1c.c. alcohol + water	22	.03331	.01560	.01771	10.65
" + 2 " + "	23	.03154	.01545	.01609	9.70
" + 4 " + "	23	.03131	.01548	.01583	9.54
" + 8 " + "	25	.03048	.01540	.01508	9.09
" + 16 " + "	25	.02930	.01550	.01380	8.32
" + 32 " + "	26	.02871	.01548	.01323	7.98
" + 50 " + "	30	.02810	.01540	.01270	7.66

TABLE IV

*Variation in the adsorption of Ba-ions by the particles of  $As_2S_3$  sol when glyccol is added in increasing conc.*

Conc. of the sol—18.89 g./litre. Radius of the particle= $75 \mu\mu$  (by extrapolation).  
Sol taken—200 c.c. Total volume =400 c.c. No. of particles in the sol taken= $6.02 \times 10^{15}$ .

Nature of sol.	N/20-BaCl <sub>2</sub> added.	Adsorption of Ba-ions			Charge e.s.u. $\times 10^6$ .
		Total.	Physical.	Chemical	
Sol + water	22 c.c.	0.02328 g.	0.01102 g.	0.01226 g.	8.60
Sol + 1c.c. glycol + water	22	.02411	.01110	.01301	9.11
" + 2 " + "	23	.02386	.01110	.01276	8.94
" + 4 " + "	25	.02343	.01100	.01243	8.71
" + 8 " + "	25	.02331	.01105	.01226	8.59
" + 16 " + "	26	.02330	.01100	.01230	8.61
" + 32 " + "	30	.02320	.01100	.01220	8.54

TABLE V

*Variation in the adsorption of Ba-ions by the particles of  $As_2S_3$  sol when glycerol is added in increasing conc.*

Conc. of the sol=20.65 g./litre. Radius of the particle= $75 \mu\mu$  (by extrapolation).  
Sol taken=200 c.c. Total volume=400 c.c. No. of particles in the sol taken= $6.58 \times 10^{14}$

Nature of sol.	N/20-BaCl <sub>2</sub> added.	Adsorption of Ba-ions			Charge e.s.u. $\times 10^6$
		Total.	Physical	Chemical.	
Sol + water	22 c.c.	0.02769 g.	0.01293 g.	0.01476 g.	9.46
Sol + 1c.c. glycerol + water	22	.02853	.01300	.01552	9.94
" + 2 " + "	23	.02850	.01300	.01550	9.93
" + 4 " + "	23	.02816	.01298	.01518	9.72
" + 8 " + "	24	—	.01290	—	—
" + 16 " + "	24	.02769	.01302	.01467	9.40
" + 36 " + "	25	.02557	.01300	.01257	8.05
" + 64 " + "	30	.02490	.01300	.01190	7.62

TABLE VI

*Variation in the adsorption of Ba-ions by the particles of arsenious sulphide sol when butyl alcohol is added in increasing concentration.*

Conc. of the sol = 19.48 g./litre. Radius of the particle =  $75 \mu\mu$  (by extrapolation).  
Sol taken = 200 c.c. Total volume = 400 c.c. No. of particles in the sol taken =  $6.206 \times 10^{14}$ .

Nature of the sol				N/20-BaCl <sub>2</sub> added.		Adsorption of Ba-ions			Charge
						Total.	Physical.	Chemical.	c.s.u. $\times 10^5$ .
Sol	+	water		22	c.c.	0.02566 g.	0.01275 g.	0.01291g.	8.79
Sol	+	1c.c. alcohol	+	22		.02408	.01286	.01122	7.62
"	+	2	"	23		.02430	.01286	.01144	7.77
"	+	4	"	23		—	.01286	—	—
"	+	8	"	24		.02524	.01280	.01244	7.77
"	+	10	"	26		.02576	.01285	.01291	8.74
"	+	13	"	26		.02632	.01275	.01357	9.22
"	+	16	"	30		.02632	.01285	.01347	9.15
"	+	24	"	30		.02500	.01280	.01220	8.29

TABLE VII

*Variation in the adsorption of Ba-ions when acetone is added in increasing concentration.*

Conc. of the sol = 21.94 g./litre. Radius of the particle =  $75 \mu\mu$  (by extrapolation).  
Sol taken = 200 c.c. Total volume = 400 c.c. No. of particles in the sol taken =  $6.99 \times 10^{14}$ .

Nature of the sol.				N/20-BaCl <sub>2</sub> added		Adsorption of Ba-ions			Charge
						Total.	Physical.	Chemical.	c.s.u. $\times 10^5$ .
Sol	+	water		23	c.c.	0.03160 g.	0.01613 g	0.01547 g	9.33
Sol	+	$\frac{1}{2}$ c.c. acetone	+	23		.03044	.01610	.01434	8.65
"	+	1	"	24		—	.01620	—	—
"	+	2	"	24		.03120	.01620	.01500	9.05
"	+	4	"	26		.03140	.01613	.01527	9.21
"	+	8	"	26		.03180	.01621	.01559	9.40
"	+	16	"	28		.03048	.01630	.01418	9.55
"	+	32	"	29.5		.03000	.01624	.01376	8.30
"	+	50	"	30		.02954	.01625	.01319	8.02
"	+	64	"	32		.02840	.01625	.01215	7.33

## DISCUSSION

From the results given in the above tables it can be seen that in the case of propyl and isopropyl alcohol, glycol and glycerol, there is a slight increase on the charge of the colloid, which is then followed by a decrease on the addition of larger amounts of non-electrolyte. In the latter condition the charge continuously falls and goes even below its original value. In the case of acetone and butyl alcohol there is a slight lowering in the initial stages, followed by an increase and then a decrease on the addition of larger amounts of non-electrolytes. In the case of propyl and isopropyl alcohols, however, stability towards coagulation concentration goes on increasing irrespective of the variation of charge, as calculated from the adsorption experiments. Further, it is interesting to note that

when coagulation concentration is plotted against the amount of non-electrolyte added, in case of propyl alcohol there is a rapid increase in stability, whereas in the case of *iso*-propyl alcohol the rate of increase is much slower. The physical adsorption almost remains constant in each case.

Out of the many factors which affect the stability of colloids on the addition of non-electrolytes, the lowering in the dielectric constant and the lowering of the solid-liquid interfacial tension are greatly emphasised. The addition of a non-electrolyte with a lower dielectric constant lowers the dielectrics of the medium. This may affect the stability in three ways : It brings about (i) a greater repulsive force between the colloidal particles on account of which the sol becomes stabilised, (ii) an increased electrical adsorption of the oppositely charged ions by the colloid, which will sensitise the sol, and (3) a repulsion between similarly charged ions, which means that they are less adsorbed and hence sensitisation results. The net effect will depend upon the magnitude of these three factors (cf. Mukherjee and Chaudhury, *J. Indian Chem. Soc.*, 1925, **2**, 307).

The decrease in interfacial tension increases stability and it is just possible that the charge may be negligible, but due to lowering of interfacial tension stability may be increased, and also a colloid, with a low charge, may be more stable than a colloid with a high charge if its interfacial tension is sufficiently low. This may explain the apparent paradox that though the charge decreases yet the coagulation concentration increases. This will specially be the case with non-electrolytes of lower surface tension.

Thus from the above it may be seen that if on the addition of the non-electrolyte a diminution of the dielectric constant accompanied by a decrease in the solid-liquid interfacial tension takes place, then we may have stability with not simultaneous increase of the charge on the colloid. But if along with these two effects, increased electrical adsorption of oppositely charged ions by the colloid also takes place, the charge may be lowered. Hence, it is possible to have stability towards electrolytic coagulation accompanied by not much variation in the charge, or even the lowering of the charge of the colloid. The net effect will depend upon the magnitude of these various factors. It appears that in the majority of cases like propyl alcohol, *isopropyl* alcohol, glycol, and glycerol, stability accompanied by a lowering in the charge is produced.

The initial increase in the charge on the addition of non-electrolytes in small concentrations is indicated by the increase in the 'chemical adsorption'. A clear conception as to how this is brought about, is not yet available. This may be due to the desorption of secondarily charged ions or a decrease in the thickness of the double layer, but certainly cannot be due to an increase in the adsorption of the similarly charged ions, because here no electrolyte is added. Attempts are being made to obtain more data to clear this point.

The initial decrease in charge in the case of acetone and butyl alcohol may be due to some complex formation between the potential bearing ions on the surface of the colloid and the non-electrolyte (cf. Kawjat, *Colloid J.*, 1939, **5**, 399).

## VARIATION OF ABSOLUTE VISCOSITY WITH TEMPERATURE.

## ORGANIC SOLUTES IN NON-AQUEOUS SOLVENTS

By A. N. BOSE

The variation of viscosity with temperature of non-electrolytes in non-aqueous solvents has been studied. It has been observed that the simple equation of Andrade,  $\log \eta = A + B/T$  is applicable to the most of the systems studied here. The values of the constants  $A$  and  $B$  of the above equation have been calculated and it has been found that  $A$  is the same both in aqueous and non-aqueous media, while  $B$  changes from solvent to solvent.

In a previous paper (Chatterji and Bose, this *Journal*, 1948, 25, 39), the variation of absolute viscosity with temperature was studied. In the present communication the same work has been extended to other systems of non-electrolytes in non-aqueous solvents.

## EXPERIMENTAL

The method employed is the same as given in the previous paper (*loc. cit.*). The results obtained are given in Table I. The viscosity was determined at four different concentrations and at several temperatures. But on account of brevity of space, the observations at the highest and at the lowest concentrations have only been recorded below. The concentrations given are expressed in g. of anhydrous solute in 100 g. of pure solvent.

TABLE I

*Viscosity of solutions at different temperatures.*

Solute	Conc	25°	30°	35°	40°	45°	50°
Solvent Methyl alcohol.							
Benzoic acid	68.0	0.01311	0.01196	0.010980	0.010140	0.009466	—
	83.0		0.013600	0.012500	0.0114700	0.010530	—
Salicylic acid	65.0	—	—	0.010490	0.009732	0.008932	0.008273
	75.0		—	0.011180	0.010360	0.009552	0.008818
Phthalic acid	24.6	—	—	0.009160	0.008445	0.007770	0.007180
	33.0		—	0.010850	0.010090	0.009326	0.008526
Cinnamic acid	37.5	—	—	0.008910	0.008453	0.007855	0.007246
	50.3		—	0.010920	0.010030	0.009163	0.008460
<i>m</i> -Nitrobenzoic acid	110.0	—	—	0.018890	0.017270	0.015730	0.014210
	156.0		—	0.027730	0.024250	0.022620	0.020260
Succinic acid	19.6	—	—	0.008055	0.007491	0.006981	0.006460
	27.8		—	0.009556	0.008870	0.008175	0.007603
Solvent = Acetone.							
Benzoic acid	56.00	0.00755	0.007075	0.006647	0.006278	0.005884	—
	62.5		—	0.007776	0.007283	0.006819	0.006407



TABLE I (contd.)

Solute.	Conc.	30°.	35°.	40°.	45°.	50°.	55°.
Solvent = Propyl alcohol.							
Benzoic acid	40.0	0.025310	0.022430	0.019880	0.017700	—	—
	56.0	0.028440	0.024980	0.022060	0.019650	—	—
Salicylic acid	43.0	—	0.022360	0.020120	0.017910	0.016020	0.01438
	54.0	—	—	0.021700	0.019290	0.017220	0.01545
Phthalic acid	10.6	—	0.021330	0.018870	0.016720	0.014880	0.01331
	5.6	—	0.017800	0.016320	0.014570	0.013020	0.01165
Cinnamic acid	18.2	—	0.020660	0.018360	0.016290	0.014520	0.01292
	30.3	—	0.021400	0.021580	0.108880	0.016830	0.01506
<i>m</i> -Nitrobenzoic acid	108.4	—	—	—	0.039510	0.031560	0.03018
	78.8	—	—	—	0.030070	0.026320	0.02324
Succinic acid	6.1	—	0.018720	0.016570	0.014920	0.013260	0.01190
	9.8	—	—	0.018880	0.016350	0.014620	0.01313
Solvent = Butyl alcohol.							
Salicylic acid	30.3	—	0.024530	0.021870	0.019510	0.017360	0.01550
	44.5	—	0.027610	0.023750	0.021540	0.019280	0.01725
Phthalic acid	4.9	—	0.023020	0.020330	0.018060	0.016040	0.01432
	7.3	—	—	0.021800	0.019280	0.017120	0.01529
Cinnamic acid	21.2	—	—	—	0.020730	0.018380	0.01638
	15.7	—	0.024800	0.021900	0.019320	0.017120	0.01532
Succinic acid	2.7	—	0.021670	0.019100	0.017040	0.015100	0.01357
	7.8	—	—	—	0.019430	0.017260	0.01541
Solvent = Nitrobenzene.							
Benzoic acid	12.0	—	0.017460	0.016260	0.015030	0.013970	0.01302
	21.0	—	—	0.017460	0.016110	0.014920	0.01393

From the results given in Table I, the following types of curves have been plotted : (1)  $\eta-t$ , (2)  $\log \eta-t$ , (3)  $\log \eta-1/T$ ; of these types of curves  $\log$  viscosity against  $1/T$  gives a more general and clearer approach to linearity like other systems studied in the previous paper. In almost all the systems the plot of  $\log \eta-1/T$  gives a straight line, except in a few systems like, methyl alcohol—benzoic acid, methyl alcohol—phthalic acid, methyl alcohol—cinnamic acid, and methyl alcohol—*m*-nitrobenzoic acid, where there is a very slight positive curvature. Hence the Andrade's equation  $\log \eta = A + B/T \dots (1)$  is applicable to the most of the systems studied here.

It is observed that in the systems of methyl alcohol and different organic acids the plot of log viscosity against  $1/T$  is not a straight line ; this may be due to the marked association of the methyl alcohol molecules as compared to the other alcohols of the same series.

From the Andrade's equation the values of the constants  $A$  and  $B$  have also been calculated. The results obtained are given in Table II.

TABLE II.

Solute.	$A$ .	$B(\rho/R)$ .	Solute.	$A$ .	$B(\rho/R)$ .	Solute.	$A$ .	$B(\rho/R)$ .
Solvent = MeOH.			Solvent = Pr OH.			Solvent = BuOH.		
Benzoic acid	-7.0951	1567	Benzoic acid	-8.0050	2310	Salicylic acid	-8.0640	2320
Salicylic acid	-7.4750	1712	Salicylic acid	-9.4100	2330	Phthalic acid	-9.4710	2448
Phthalic acid	-7.3970	1690	Phthalic acid	-9.4240	2410	Cinnamic acid	-9.5146	2468
Cinnamic acid	-7.7790	1809	Cinnamic acid	-9.6989	2514	Succinic acid	-9.3091	2375
<i>m</i> -Nitrobenzoic acid	-8.0660	2020	<i>m</i> -Nitrobenzoic acid	-10.106	1700	Solvent Acetone.		
Succinic acid	-8.1554	1887	Succinic acid	-9.0560	2280	Benzoic acid	-5.8840	1132
						Solvent Nitrobenzene.		
						Benzoic acid	-7.5790	1816

The value of  $A$  for different systems is almost constant and has the same numerical value as those of the systems already studied in the previous paper. If in the equation of Andrade we take the value of  $T$  as infinity then  $\log \eta = A$ , i.e., the viscosity of the infinite temperature is nearly the same in all the systems, aqueous or non-aqueous.

The value of  $B$  appears to be the characteristic of the solvent, e.g. for the systems of methyl alcohol it is nearly 1800, for propyl and butyl alcohol it is between 2300 and 2500. This may be due to the presence of  $\text{CH}_2$  group in between  $\text{CH}_3$  and  $\text{OH}$  group and thus making the  $\text{OH}$  group less active.

The author wishes to express his most sincere thanks to Dr. A. C. Chatterji for his valuable suggestions and guidance in this work and to the U.P. Government for the grant of a research fellowship.

## INFLUENCE OF CONCENTRATION ON THE PROPERTIES OF ARABIC ACID SOLUTION

By S. N. MUKHERJEE AND K. B. GHOSH

Arabic acid solution is a polydisperse system consisting of micelles of different states of aggregation. The trend of the changes of the properties with concentration studied here indicates that there is probably a formation of aggregates in this system too, but such phenomenon does not appear to begin abruptly at any particular concentration. Rather it is more probable that the process of aggregation is progressive, right from very low concentrations. Although there appear breaks in the curves showing variation of different properties as functions of concentration, these do not all occur at the same concentration.

Gum arabic occurs in nature as an exudate of *Acacia arabica* (Beng., Babla). As isolated by usual methods it consists mostly of the salt of a complex acid with potassium, calcium and magnesium (cf. O'Sullivan, *J. Chem. Soc.*, 1884, **45**, 41) as inferred from the nature of the ash obtained by incinerating the purified gum. By hydrolysing the gum with sulphuric acid O' Sullivan obtained a pentose sugar (arabinose), a relatively small quantity of hexose (galactose) and an acid which he termed "arabic acid." More recent work shows that this acid consists of a compound of *d*-glycuronic acid and galactose containing other carbohydrate molecules (*d*-galactose, *l*-arabinose and rhamnose) attached to it by glycosidic binding (Butler and Cretcher, *J. Amer. Chem. Soc.*, 1929, **51**, 1519; Norman, *Biochem. J.*, 1929, **23**, 24, 524; Weinmann, *Ber.*, 1929, **62**, 1637). This acid kernel has been known as the galactose-glycuronic acid (more generally as aldobionic acid) the constitution and composition of which have been investigated in a comparatively recent work by Hotchkins and Goebel (*J. Amer. Chem. Soc.*, 1936, **58**, 858).

Properties of this acid in aqueous solution present some peculiar features which were looked upon by the earlier workers as difficult of explanation and attributed to the colloidal nature of the solution. Thomas and Murray (*J. Phys. Chem.*, 1928, **32**, 676) carried out systematic investigations on its electrochemical and osmotic properties in solution. More recently Pauli and Ripper (*Kolloid Z.*, 1933, **62**, 162) as well as Pauli and Palmrich (*ibid.*, 1937, **79**, 63), Taft and Malm (*J. Phys. Chem.*, 1931, **35**, 874), and Briggs (*ibid.*, 1934, **38**, 867) have made important contributions to our knowledge of the electrochemical properties of the acid hydrosol prepared and purified by electrodialysis. Kruyt and Tendeloo (*Koll.-Chem. Beih.*, 1929, **29**, 396) from viscosity measurements in presence and absence of electrolytes have concluded that the aqueous solution of the gum acid has the characteristics of a lyophilic colloid. Pauli and Ripper (*loc. cit.*) have suggested that the ionogenic part of the complex glycuronic acid, viz., the carboxyl group, imparts a negative charge to the sol particles by its electrolytic dissociation, whereas the attached carbohydrate groups principally behave as the neutral part whose hydration imparts lyophilic character to the sol.

The arabic acid in aqueous solution has thus been looked upon as a colloidal electrolyte. Physical properties, specially electrochemical properties of the hydrosols of colloidal electrolytes show characteristic variations with concentration as has been shown by McBain and co-workers (McBain and Betz, *J. Amer. Chem. Soc.*, 1935, **57**, 1909), Lottermoser and Puschel (*Kolloid Z.*, 1933, **63**, 175) and Hartley and co-workers (vide the summarising paper, *Kolloid Z.*, 1939, **88**, 22). A study of the nature of these variations

has undoubtedly served to elucidate the state of aggregation of the particles existing in such sols and also to understand the anomalous electrochemical and osmotic properties of a number of such substances. The present work aims at an investigation into the influence of concentration on different properties of the aqueous solution along this line and at a correct assessment of the role of the colloid character of the solution upon its behaviour.

## EXPERIMENTAL

Acid sols used in the present investigation were prepared by purification and hydrolysis of the gum in the following manner.

Gum arabic (Merck Alniss,  $p_H$  VII; 30 g.) was dissolved in 250 c. c. of equilibrium water ( $1.2 \times 10^{-6}$  mho at  $35^\circ$ ) and filtered; 30 g. of NaCl of reagent quality were added to it and dissolved by shaking; the resulting sodium salt was then precipitated out by addition of 700 c. c. of rectified spirit and separated by filtration. The residue was then pressed between filter papers, dissolved again in 150 c. c. water and 17 g. of NaCl were added to it. The sodium salt was once again precipitated by excess of alcohol. This process of solution and precipitation of the Na salt was repeated several times in order to remove completely the basic radicals, e.g., K, Ca and Mg. Three such repetitions were found sufficient for the purpose (cf. Bungenberg de Jong and Teunissen, *Koll.-Chem. Beih.*, 1938, **47**, 254).

The sodium salt was next dissolved in 100 c.c. of water mixed with about 50 c.c. 3*N*-HCl and the salt precipitated again by 500 c. c. of rectified spirit, filtered, the residue washed with 75% alcohol till free from chlorine, and then with alcohol-water mixture (50:50) several times. The residue was then dried at room temperature ( $30^\circ$ ) on a clock glass.

The purified acid, thus obtained, was preserved in the solid state in a well cleaned resistance glass bottle from which 1% sol was prepared by weighing out the requisite amount in equilibrium water and shaking it thoroughly in a mechanical shaker for half an hour. The resulting sol was preserved in similar bottles, sterilised by continued steaming, under a layer of toluene. The  $p_H$  and specific conductance were found to remain constant in presence of toluene. After four weeks a slight turbidity appeared, but no other change was indicated.

After six weeks, however, the  $p_H$  and specific conductance of the sol indicated definite signs of change ( $p_H$  changed from 2.95 to 2.71 and sp. conductance from  $4.50 \times 10^{-4}$  to  $4.75 \times 10^{-4}$  mho). The sols used in the present investigation were in no case four weeks old and different samples were prepared. The purified solid appeared to suffer a loss of peptisability with time and each time the starting sol was made from freshly prepared gum acid. Consequently it was ascertained by experiments that the sols were comparable with each other so far as the properties studied in the present investigation were concerned provided they had the same acid contents (cf. Taft and Malm, *loc. cit.*).

The acid used for preparation of the sol was tested before for nitrogen, phosphorus, sulphur and chlorine and also for reducing sugars. Specific rotation was  $-27^\circ$  and the ash content, 0.12%. These properties compare very favourably with those of previous workers.

The effect of concentration was mainly studied with respect to (i) ultrafiltration, (ii) specific conductance, (iii) free and total acidity, (iv) dissociation constant and (v) cataphoretic velocity.

Hydrogen-ion activity and total acidity were determined electrochemically by titration with NaOH with a hydrogen electrode. The platinum deposit of the electrode was removed and replatinisation done every day after measurements to avoid erratic behaviours of the electrode (vide Mukherjee *et al.*, *Indian J. Agric. Sci.*, 1936, **6**, 517).

To ascertain whether equilibrium between the gum acid and the base has been attained in potentiometric and conductometric titrations within the usual time allowed in such experiments, the same volume of the sol (10 c. c.) as used in these experiments was taken in a series of Jena bottles, mixed with corresponding amounts of the base and kept for 24 hours after which the specific conductance and  $p_H$  of these samples were determined. The results obtained indicated that the equilibrium in the interaction of the acid with NaOH was reached within a short time (cf. Briggs, *loc. cit.*). Cataphoretic velocity (C. V.) was measured in the same manner as reported in a previous paper by the author (cf. Mukherjee and Sarkar, this *Journal*, 1947, **24**, 65).

## DISCUSSION

*Ultrafiltration.*—The sol was observed not to pass through a parchment nor a celloidion membrane during dialysis but it could be ultrafiltered through celloid membrane No. 600, under pressure. The process was, however, extremely slow. The ultrafiltrate presented an appearance similar to that of the parent sol; its specific conductance was high being of the same order as that of the sol from which it was derived. The total acidity as determined by titration with NaOH was also high being about 50% of the parent sol. Whether the acid in the ultrafiltrate was present in true solution could not, however, be ascertained *a priori*. Ultramicroscopic examination revealed the presence of a large number of particles executing brisk Brownian movement. Their number was observed to be smaller than that in the parent sol as determined by a preliminary counting.

TABLE I

*Arabic acid solution.*

Temp. =  $35^\circ$

Conc. (g./litre)	Sp. cond. $\times 10^4$ mho.	Sp. cond. of ultra- filtrate $\times 10^4$ mho.	Conc. (g./litre)	Sp. cond. $\times 10^4$ mho.	Sp. cond. of ultra- filtrate $\times 10^4$ mho.
1.12	0.75	0.67	2.25	1.75	0.92
1.40	0.90	0.75	3.60	2.30	1.50
1.80	1.30	0.80	9.40	2.37	1.72

Sols of different concentrations were ultrafiltered and in every case a difference in the specific conductance between the sol and its ultrafiltrate was observed to exist. Although the difference became gradually smaller with decreasing concentration, it persisted even up to the lowest concentration observed by us (vide Table I).

These observations, however, bring out that arabic acid sol is a polydisperse system which contains particles of different size. Further corroboration is obtained from the observation that the sol also contains particles of microscopic size which are visible by an ordinary microscope with magnification of about  $\times 600$ .

*Specific and Equivalent Conductance.*—The relevant data have been presented in Table II.

TABLE II

*Arabic acid solution.*

Temp.  $-35^{\circ} \pm 0.1^{\circ}$ . Sp. cond. of water used  $-1.1 \times 10^{-6}$  mho at  $35^{\circ}$ .

Conc. in g./l. (c)	$\sqrt{c}$	Sp. cond. ( $\kappa$ ) obs. $\times 10^{-4}$ mho.	$\alpha_H$ calc. from $p_H$	Sp. cond. calc. from $\alpha_H \times 10^{-4}$ mho.	Equiv. cond. ( $\Lambda$ ) per g./litre.
0.25	0.50	0.186	0.32	0.138	$7.44 \times 10^{-2}$
0.40	0.63	0.288	0.65	0.260	7.20
0.90	0.95	0.594	1.48	0.592	6.60
1.50	1.30	0.730	2.00	0.800	4.20
4.00	2.00	1.800	6.60	2.640	4.50
7.00	2.70	3.240	10.50	4.200	4.60
8.00	2.80	3.540	11.10	4.500	4.50

Since the variations in specific conductance do not show any point of particular interest and hence these have not been graphically shown. Instead, the equivalent conductance derived from these have been shown in Fig. 1 against square root of concentration. Since these acids (as will be shown in a future communication) have no fixed total acidity which has been observed to show variations with the nature of the bases used for inter action, it is difficult to estimate the equivalent weight of arabic acid, and so the equivalent conductance cannot be calculated as in ordinary acids. In this case therefore a quantity ( $\Lambda$ ) has been defined as the conductance offered by a solution sufficient in volume to contain 1 g. of the acid and placed between two electrodes of indefinite size (cf. Mukherjee and Sarkar, *loc. cit.*).

Fig. 1

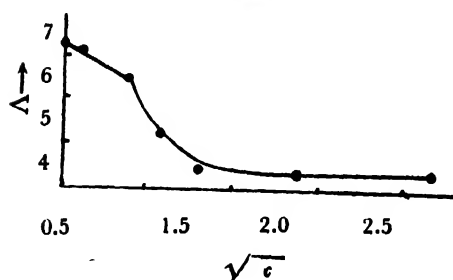
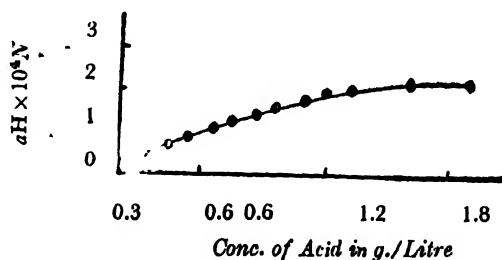


Fig. 2.



This will be strictly proportional to the equivalent conductance. The  $\Lambda-\sqrt{c}$  curve, according to Onsager's equation

$$\Lambda^c = \Lambda^\circ - k\sqrt{c}$$

(where  $\Lambda^\circ$  stands for the equivalent conductance at infinite dilution and  $k$  is a constant) should be a straight line sloping downwards with increase in  $\sqrt{c}$ . The graph as shown in Fig. 1 is, however, not a straight line but a curve sloping downwards with a kink at a concentration of about 0.8 g. of the acid per litre. The curve, however, reaches almost a constant value at higher concentration and does not show any minimum.

The kink observed in the  $\Lambda-\sqrt{c}$  curves at low concentrations has been looked upon as indications of aggregate formation in solutions of colloidal electrolytes like soap solutions and solutions of the salts of different long chain fatty acids and long chain sulphonic acids (cf. McBain, *loc. cit.* Lottermoser and co-workers, *loc. cit.* Hartley, *loc. cit.*). A similar line of argument would also suggest the existence of aggregate formation in this case as well. This aspect will be judged in the light of evidences obtained from behaviour of other properties in the following sections.

It will not be irrelevant to raise one pertinent question in this connection as to whether the Onsager's equation can be applied to the present system. The Debye-Hückel interionic attraction theory, of which Onsager's equation forms only an extension, assumes complete dissociation of the electrolyte which is far from true in the present system, as evident from its low specific conductance. The assumption of spherical symmetry, which is another important point on which the calculations are based, cannot be justified in the present case, since here even the simple anions are much larger and mostly consist of sugar molecules with an ionisable carboxyl group situated at one end. The distribution of counter ions (H-ions) is far from uniform or symmetrical round each anion. And although it can be visualised that hydrogen ions are distributed round each anion, it is difficult to visualise how micellar anions will be distributed round each hydrogen-ion which is an important assumption in the interionic attraction theory. Moreover, the hydration of the carbohydrate part makes the picture more complex.

It will so be observed that the values of specific conductance are low indicating a low degree of dissociation of the acid. Another interesting feature is that the observed values of specific conductance are much lower than those obtained by calculation from the hydrogen-ion activity alone of the solution as determined from its  $p_H$  (vide column 5 of Table II) at higher concentrations but become almost equal in dilute solutions. Thus in the arabic acid solution there exists a discrepancy between the hydrogen-ion activity and specific conductance. It is, however, difficult to visualise how hydrogen ions, which register their potential (*i.e.*, are active), fail to contribute to specific conductance. This is also against the accepted views in electrochemistry. Probably the assumption of independent migration of ions, on which these calculations are based, is responsible for such anomalies. If, however, a lower value of ionic conductance be assumed for H-ions due to interionic attractions, the corrections introduced are expected to remove the discrepancy to a certain extent.

**Free and Total Acidity.**—The free acidity ( $a_H$ ) or the hydrogen-ion activity has been calculated from the  $p_H$  values determined potentiometrically. The total acidity ( $c$ )

has been worked out from the potentiometric titration of the acid with NaOH. The data appear in Table III.

TABLE III

*Arabic acid solution.*

Temp. =  $35 \pm 0.1^\circ$ .

Conc. (g./l.)	$p_H$ .	Free acidity $a_H \times 10^4 N.$	Total acidity $c_H \times 10^4 N.$	$a_H/c_H$ ratio ( $=f$ ).	Total acidity $\times 10^4 N$ (conductometric)
0.33	4.26	0.55	2.80	0.197	—
0.44	4.16	0.70	3.80	0.184	3.72
0.55	4.05	0.89	4.80	0.185	4.83
0.66	3.99	1.02	5.60	0.182	5.58
0.77	3.91	1.23	7.00	0.186	6.96
0.88	3.83	1.48	7.60	0.190	7.55
0.99	3.79	1.60	8.60	0.186	—
1.10	3.78	1.66	9.50	0.179	—
1.21	3.75	1.76	10.5	0.167	—
1.32	3.72	1.92	11.4	0.168	11.29
1.43	3.70	1.96	12.3	0.160	12.29
1.65	3.68	2.10	14.3	0.149	14.10
1.89	3.68	2.08	17.1	0.121	16.95
2.20	3.38	2.21	19.0	0.115	18.90

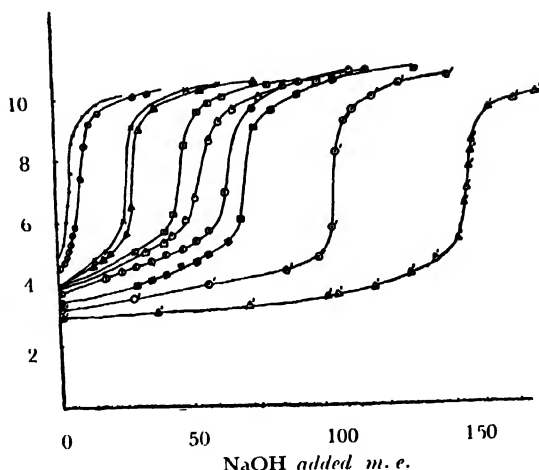
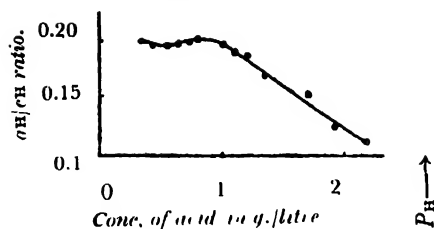
The variations of  $a_H$  with concentration ( $c$ ) have been presented in Fig. 2. The curve shows a progressive increase with concentration and runs smooth. A close scrutiny of the total acidities ( $c_H$ ) from column 4 of Table III will show that they vary linearly with concentration, which signifies that the total acidity per g. of the acid does not change with concentration.

Thus the absence of any break in these curves does not help very much in supplying any evidence with regard to the formation of aggregates in the system. The ratio of free to total acidity ( $a/c_H = f$ ) (shown in column 5, Table III) was therefore drawn against concentration with a view to bringing in further analysis of these data. The curve, shown in Fig. 3, evidently passes through a small minimum followed by a maximum at low concentrations. The sharp decrease beyond the maximum occurs at a concentration of about 0.9 g./litre and it decreases steadily at higher concentrations.



Fig. 4

Fig. 3

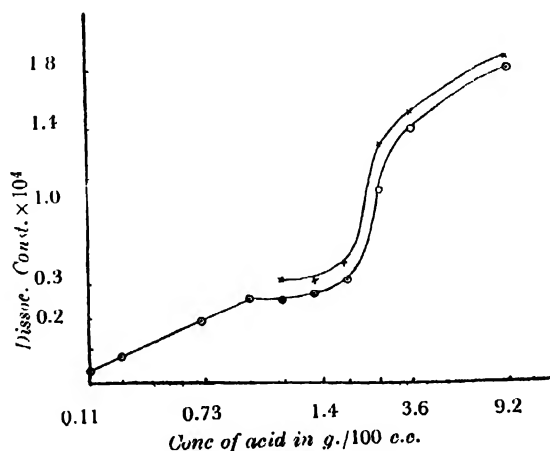
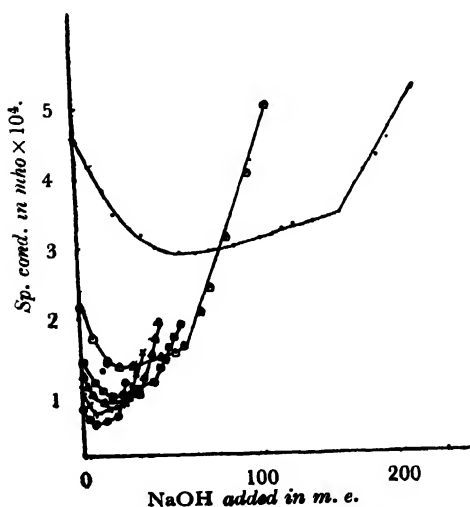


The potentiometric titration curves with NaOH from which the total acidities were determined as shown in Fig. 4, present the characteristic features of a strong acid at higher concentrations. With increasing dilution the initial flat portion of the curve tends to be smaller and smaller, thus simulating the features of weak acids to a certain extent. The  $pH$  of neutralisation, however, varies very little with concentration and occurs in close vicinity of  $pH$  7, which is again a characteristic feature of strong acids.\*

Conductometric titration curves (Fig. 5), however, show two inflexion points. At first the specific conductance diminishes rapidly with the addition of the alkali, and beyond the first inflexion it tends to increase to a certain extent till the second inflexion is reached, after which the curve has a steeper and linear rise corresponding to the alkali line. The first inflexion point in the conductometric titration curve approximately corresponds to the neutralisation of free acidity (hydrogen-ion activity) as obtained from  $pH$  measurements.

Fig. 5

Fig. 6



\* This aspect will be dealt with in details in a subsequent communication on the "Interaction of arabic acid with bases".

The second inflexion point followed by the alkali line probably indicates the neutralisation of the total acid. Compared with potentiometric titration data (column 6, Table III) values of total acidity obtained for corresponding concentrations by the conductometric method show fair agreement. Equivalent weight of the acid, as calculated from the base required for complete neutralisation, comes out to be 1184 approximately which shows a satisfactory agreement with the value of 1175 obtained by Thomas and Murray (*loc. cit.*) and 1210 observed by Bungenberg de Jong (*loc. cit.*). The base required for neutralisation of 1 g. of the acid has been calculated to be  $84.4 \times 10^{-3}$  equivalents of NaOH.

*The Dissociation Constant.*—The dissociation constant of the acid cannot obviously be calculated from the potentiometric titration curves, as they resemble those of strong acids and Henderson's equation for calculation of  $pK$  cannot be applied. From conductometric titrations the dissociation constant can be calculated if we remember that the first inflexion point of such curves gives the free acidity which, may roughly be taken to be the hydrogen-ion concentration and that the concentration of the anions is equal to the hydrogen-ion activity or free acidity of the solution. With these assumptions the dissociation constant,

$$K = \frac{(C^1H)^2}{C_H - C^1H} \quad \text{where } C \text{ stands for the hydrogen-ion concentration at the first } C_H - C^1H \text{ inflexion.}$$

The values of  $K$  obtained in this way are given in Table IV.

Table IV.

Conc. of acid (g./litre).	Dissociation constant $\times 10^5$ .	Conc. of acid (g./litre).	Dissociation const $\times 10^5$ .
0.11	0.398	1.40	3.0*
0.22	0.79	1.80	3.7*
0.73	1.80	2.25	13.1
0.90	2.5*	3.60	17.7
1.12	2.5*	9.4	29.6

The dissociation constants have an order of  $10^{-5}$  which indicates a weak character of the acid, while the potentiometric titration curves resemble those of strong acids. Again, the dissociation constant exhibits variation with concentration for which reason it is more or less a misnomer to call it a constant. The nature of the variations has been shown in Fig. 6. The curve shows a slow increase at lower concentrations followed by a region of constant value (0.90 to 1.80 g./litre marked by asterisks in Table IV). Beyond this region the curve shoots up, followed again by a region of slow but steady rise. The experiment was repeated in a second specimen, the curve for which runs almost parallel to the previous one.

The diminution of the slope of the curve at higher concentrations is suggestive of a tendency to reach a constant value at still higher concentrations. Pauli and Palmrich (*loc. cit.*), however, observed a steady increase of the dissociation constant with a tendency

to reach a constant value at higher concentrations. Their observations, however, did not extend to low concentrations, and hence they missed the peculiar nature of the variation of this property.

Two different view points have, however, been advanced by Pauli and co-workers (*loc. cit.*). Valko (*Kolloid Z*, 1930, **51**, 130) has suggested that the dissociation constant, which is a ratio of the two velocity constants (*viz.*, those of the forward and backward reactions of the reversible dissociation process), must be influenced by a change in one or both the velocity constants. In a binary dissociation process, if it be assumed that one of the products of dissociation be congealed or removed due to association to form bigger micelles, the rate of the reverse reaction will be considerably diminished due to diminished chances of collision. This will tend to increase the value of  $K$ . In the light of these observations the increase of  $K$  should be due to aggregate formation proceeding in this case, and since this increase of  $K$  goes on right from very low concentrations, it may be inferred that aggregation also proceeds in this system from low concentrations as well.

The second view point was proposed by Briggs (*J. Phys. Chem.*, 1934, **38**, 867) who regards the acid as a polybasic one the dissociation of which in aqueous solution does not proceed in a simple and uniform manner like that of a monobasic acid at all concentrations. At higher concentrations the primary dissociation becomes prominent, at lower concentrations the secondary, tertiary and other types of dissociation may appear which are generally of weak character. He cites the nature of the potentiometric titration curves in support of his views, but this does not appear to be plausible as these curves resemble those of strong monobasic acids, rather than a polybasic acid having dissociation constants separated from one another by a narrow margin. Assuming the theory of widely separated charges as proposed by Simms (*J. Amer. Chem. Soc.*, 1926, **48**, 1239, 1251) the monobasic nature of the potentiometric titration curves can be understood as the result of aggregation or association, in which case also the successive stages of the dissociation of the acid cannot be looked upon as being the same as the dissociation of a polybasic acid in successive stages.

Hence, the plausible conclusions from the variation of  $K$  with concentration are that probably some type of aggregation proceeds within the system as proposed by Valko (*loc. cit.*). As to the shape and nature of the potentiometric titration curves the discussion is postponed until further work is done on the interaction of this acid with bases.

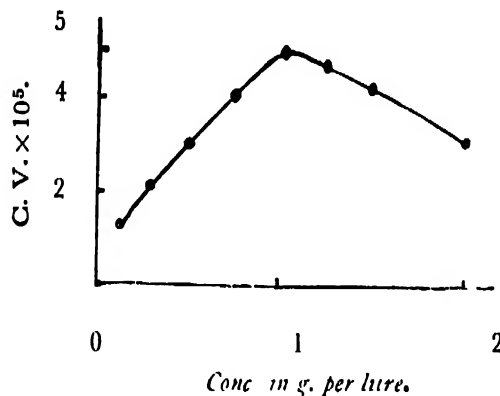
**Cataphoretic Velocity (C. V.).**—Results of cataphoretic measurements in the case of arabic acid in the same way as referred to in a previous paper by one of the authors (*vide* Mukherjee and Sarkar, *loc. cit.*) have been presented in Table V and graphically shown in Fig. 7.

TABLE V

Conc. (g/litre).	C.V. $\times 10^4$	Conc. (g/litre).	C.V. $\times 10^4$ .
0.125	1.2	1.50	4.2
0.25	2.0	2.00	2.9
0.50	2.9	4.00	2.2
0.75	4.0	8.00	1.25
1.00	5.0	10.0	1.60

The curve evidently exhibits a maximum at a concentration of 1.0 g./litre, which is quite close to the concentration where  $\Lambda-\sqrt{c}$  and  $a_H/c_H-c$  curves exhibit their breaks (about 0.9 g./litre in Figs. 1 and 3). The increase in C. V. indicates an increase in con-

Fig. 7



ductance on the part of the micelle anion. Hartley (*loc. cit.*) reports a rise of equivalent conductance of the micelle ions in his system, and McBain (*loc. cit.*) reports a rise of transport number above unity in Na-soap solutions. Both of them have explained their observations as due to the formation of aggregates on the part of the paraffin chain ions to form micelles. In the present system, since an increase in C.V. is observed from very low concentrations (even below that indicated as the critical concentration from the  $\Lambda-\sqrt{c}$  curves) a progressive aggregate formation right from low concentrations appears to be suggestive. The cause of a decrease of cataphoretic velocity is not, however, properly understood. More work seems to be essential for a definite conclusion on this point.

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# VARIATION OF RELATIVE VISCOSITY WITH TEMPERATURE. ORGANIC SOLUTES IN NON-AQUEOUS SOLVENTS

By A. C. CHATTERJI AND A. N. BOSE

The variation of relative viscosity with temperature has been studied. In most of the systems studied here the value of  $\frac{\delta}{\delta t} \left( \frac{\eta_s}{\eta_o} \right)$  is negative but for the systems of butyl alcohol-phthalic acid, butyl alcohol-succinic acid, and propyl alcohol-succinic acid the value of  $\frac{\delta}{\delta t} \left( \frac{\eta_s}{\eta_o} \right)$  is almost zero at lower concentrations. This may be due to the fact that the molecules of butyl alcohol and propyl alcohol are less associated than the molecules of methyl alcohol.

In a previous communication (Chatterji and Bose, this *Journal*, 1948, **25**, 91) the variation of relative viscosity with temperature has been studied. In this paper the same work has been extended to other systems of organic solutes in non-aqueous solvents

## EXPERIMENTAL

The method employed is the same as in the previous paper. Results calculated from the viscosity data, thus obtained, are given in Table I.

TABLE I

Solute.	Conc. (g./100 g.)	25°.	30°.	35°.	40°.	45°.	50°.	55°.
Solvent: Methyl alcohol.								
Benzoic acid	68.0	2.373	2.300	2.253	2.221	2.201	—	—
	83.0	—	2.614	2.564	2.512	2.448	—	—
Salicylic acid	65.0	—	—	2.153	2.131	2.077	2.040	—
	75.0	—	—	2.292	2.269	2.221	2.190	—
Phthalic acid	33.0	—	—	2.228	2.208	2.170	2.116	—
	24.6	—	—	1.879	1.850	1.806	1.783	—
Cinnamic acid	37.5	—	—	1.900	1.852	1.827	1.798	—
	50.3	—	—	2.242	2.196	2.132	2.208	—
<i>m</i> -Nitrobenzoic acid	110.0	—	—	3.863	3.782	3.658	3.528	—
	156.0	—	—	5.031	5.260	5.421	5.690	—
Succinic acid	19.6	—	—	1.653	1.641	1.624	1.604	—
	27.8	—	—	1.960	1.943	1.901	1.887	—

TABLE I (contd.)

Solute.	Conc. (g./100 g.)	25°.	30°.	35°.	40°.	45°.	50°.	55°.
Solvent = Propyl alcohol.								
Benzoic acid	68.2	—	—	—	1.686	1.680	1.670	1.650
	42.2	—	—	1.456	1.448	1.438	1.428	1.411
Salicylic acid	54.0	—	—	—	1.545	1.527	1.525	1.507
	43.0	—	—	1.435	1.432	1.426	1.417	1.403
Phthalic acid	10.6	—	—	1.359	1.344	1.331	1.316	1.299
	5.6	—	—	1.173	1.167	1.160	1.151	1.138
Cinnamic acid	30.3	—	—	1.555	1.536	1.504	1.490	1.456
	18.2	—	—	1.316	1.308	1.296	1.285	1.260
<i>m</i> -Nitrobenzoic acid	108.4	—	—	—	—	3.146	3.057	2.945
	78.8	—	—	—	—	2.393	2.330	2.263
Succinic acid	6.1	—	—	1.118	1.118	1.118	1.1173	1.1170
	9.8	—	—	—	1.309	1.302	1.294	1.283
Solvent = Butyl alcohol.								
Salicylic acid	44.5	—	—	1.373	1.364	1.355	1.366	1.355
	30.3	—	—	1.220	1.229	1.229	1.230	1.220
Phthalic acid	4.9	—	—	1.142	1.141	1.136	1.136	1.135
	7.3	—	—	—	1.224	1.213	1.213	1.207
Cinnamic acid	21.2	—	—	—	1.315	1.304	1.300	1.288
	15.7	—	—	1.235	1.228	1.214	1.213	1.207
Succinic acid	2.7	—	—	1.077	1.071	1.071	1.070	1.069
	7.8	—	—	—	—	1.222	1.223	1.214

## DISCUSSION

It has been suggested in the previous paper that if the solvent consists of associated molecules and the solute forms solvates with the solvent molecules, the value of  $\delta/\delta t(\eta_s/\eta_o)$  should be either positive or negative, depending upon which of the two factors, viz. depolymerisation of the solvent molecules or breaking up of the solvate complexes predominates. From the results given in Table I it is observed that for almost all the systems studied here, the value of  $\delta/\delta t(\eta_s/\eta_o)$  is negative except for the systems of butyl alcohol—phthalic acid, butyl alcohol—succinic acid and propyl alcohol—succinic acid the value of  $\delta/\delta t(\eta_s/\eta_o)$  is almost zero at lower concentrations.

As in this paper highly concentrated solutions have been taken, the effect of depolymerisation of the solvent molecule is negligible as compared to the breaking up of the solvate complexes, and therefore the value of  $\delta/\delta t(\eta_s/\eta_o)$  for these systems are negative.

If we examine the systems studied here, we find that for the systems where the solvent has got low value for dipole moment *i.e.* where the association of the solvent molecule is less, the negative value of  $\delta/\delta t(\eta_s/\eta_o)$  is less than the solvents where the association of the solvent molecule is more marked. In case of the systems of methyl alcohol, the negative value for  $\delta/\delta t(\eta_s/\eta_o)$  is much more than the systems for propyl alcohol which in turn is more than the systems of butyl alcohol. The dipole moment of butyl alcohol is greater than that of propyl alcohol which again is greater than that of methyl alcohol.

For the systems of butyl alcohol the value of  $\delta/\delta t(\eta_s/\eta_o)$  is zero in some cases, it is just possible that for the systems of higher alcohols the value may be also zero.

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## SUPERSATURATION LIMITS OF NON-AQUEOUS SOLUTIONS.

## PART I

By A. C. CHATTERJI AND A. N. BOSE

Limits of supersaturation in non-aqueous solutions of non-electrolytes have been studied. The value of  $(T_s - T)\lambda$  has been calculated. From the value of  $(T_s - T)\lambda$  the value of the radius of the stable crystal nucleus has been calculated. The value of ' $r$ ' has got the same order in different systems *i.e.*, the order is  $10^{-6}$  cm.

The effect of heating on the limits of supersaturation of non-aqueous solutions of non-electrolytes has been studied. The effect of heating is observed in most of the systems. The product of concentration ( $c$ ) and the fluidity ' $\phi$ ' has been calculated. It is found for the systems having ' $c\phi$ ' value more than 30, heating effect is negligible. Certain exceptions to the ' $\phi$ ' rule are noticed. These are accounted for by the low mutual affinity among the molecules of the solutes.

In a number of papers published by Ram Gopal from this laboratory (this *Journal*, 1943, *et seq.*), it has been shown that  $(T_s - T)$  is fairly constant in aqueous solutions of some electrolytes. In other cases  $(T_s - T)$  has, however, been found to increase with successive heating and cooling. It has also been observed that there is a third type of aqueous solution which does not crystallise even after sufficient cooling. Further, it has been observed that in general  $(T_s - T)$  increases with heating in the case of a number of aqueous solutions. In this paper an attempt has been made to find out if these generalisations are also applicable to solutions of non-electrolytes in non-aqueous solvents.

We have here classified our data into three different types. Table I shows those with very little or no heating effect. Table II shows those with heating effect, *i.e.* in these systems  $(T_s - T)$  increases with successive heating and cooling. In order to find out the value of  $(T_s - T)$  the first temperature of spontaneous crystallisation has been taken as other values of  $(T_s - T)$  are increased due to heating effect. In Table III there are, however, certain types that do not spontaneously crystallise even on considerable cooling.

## EXPERIMENTAL

The experimental method followed is the same as that of Ram Gopal (*J. Indian Chem. Soc.*, 1943, 20, 187). Results obtained are given below in Tables I, II and III.

TABLE I

Solute.	Solvent.	Temperature range studied.	$(T_s - T)$ (average).	Remarks.
1. Naphthalene	Carbon tetrachloride	25°, 30°, 35°, 40°, 45°, 50°	2.9	No heating effect after heating for 11 hours.
2. <i>m</i> -Dinitrobenzene	Bromobenzene	50°, 55°, 60°, 65°, 70°, 75°	10.5	„
3. <i>p</i> -Dibromobenzene	Propyl alcohol	50°, 55°, 60°, 65°, 70°	10.2	„
4. Anthracene	Benzene	45°, 50°, 55°, 60°, 65°, 70°	7.9	„
5. Naphthalene	Aniline	30°, 35°, 40°, 45°, 50°, 55°	9.2	„



TABLE II

Solute.	Solvent.	Temperature range studied.	( $T_s - T$ ) (average)	Remarks.
1. Naphthalene	Benzene	30°, 35°, 40°, 45°, 50°, 55°	5.6	Heating effect after heating for 3 hours but after that $T$ does not change even after heating for 11 hours.
2. Naphthalene	Chlorobenzene	35°, 40°, 45°, 50°, 55°, 60°	4.3	„
3. „	Nitrobenzene	30°, 40°, 45°, 50°, 55°, 60°	7.9	„
4. „	Toluene	35°, 40°, 45°, 50°, 55°, 60°	5.5	„
5. „	Methyl alcohol	25°, 30°, 35°, 40°, 45°	1.3	„
6. „	<i>n</i> -Butyl alcohol	35°, 40°, 45°, 50°, 55°, 60°	13.5	„
7. „	Acetic acid	30°, 35°, 40°, 45°, 50°, 55°	7.4	„
8. Acenaphthene	Chloroform	35°, 40°, 45°, 48°, 50°, 52°	16.6	„
9. Diphenyl	Benzene	35°, 40°, 45°, 50°, 55°	15.6	Heating effect
10. Acenaphthene	<i>n</i> -Propyl alcohol	40°, 45°, 50°, 55°, 60°	18.0	„
11. Benzoic acid	Benzene	50°, 55°, 60°, 65°, 78°, 83°	8.0	„
12. Salicylic acid	Benzene	45°, 50°, 55°, 60°, 65°, 70°	10.0	„
13. <i>p</i> -Dibromobenzene	Benzene	40°, 45°, 50°, 55°, 60°, 65°	16.8	„
14. <i>m</i> Dinitrobenzene	Benzene	55°, 60°, 65°, 70°, 75°, 80°	22.2	„
15. Acenaphthene	Toluene	45°, 50°, 55°, 60°, 65°, 70°	25.0	„
16. Benzoic acid	Toluene	55°, 60°, 65°, 70°, 75°, 80°	19.1	„
17. „	Acetone	45°, 50°, 55°, 57°, 60°	12.5	„
18. Acenaphthene	Methyl alcohol	30°, 35°, 40°, 45°, 50°	10.1	„
19. <i>p</i> -Dibromobenzene	Bromobenzene	45°, 50°, 55°, 60°, 65°, 70°	11.5	„
20. Acetanilide	Chloroform	45°, 50°, 52°, 55°	23.2	„

TABLE III

Methyl alcohol—Acetanilide,      Methyl alcohol—Diphenylamine,      Hexane—Diphenylamine,  
 Acetone—resorcinol.

From the above results it has been tested whether the expression, which has been deduced from the equation of Jones and Partington (*Phil. Mag.*, 1915, **29**, 35), remains constant in these systems also,

Results for the expression  $(T_s - T)$  are given in Table IV.

TABLE IV

Solution		$\lambda$ in	$(T_s - T)$	$(T_s - T)$
Solvent.	Solute.	kilo Joules.	(°C)	(in calories).
1. Benzene	Naphthalene	18.5	5.6°	24670
2. "	Benzoic acid	14.2	8.0	27050
3. Toluene	Naphthalene	17.8	5.5	23450
4. Methyl alcohol	"	17.7	4.3	18130
5. Acetone	Benzoic acid	12.1	12.5	36020
6. Acetic acid	Naphthalene	17.5	7.4	30740
7. Aniline	"	19.8	9.2	43400
8. Benzene	Salicylic acid	23.9	10.0	56910
9. "	Diphenyl	18.0	15.6	66860
10. Toluene	Benzoic acid	14.2	19.1	64600
11. Chloroform	Acenaphthene	18.8	16.6	74310
12. Methyl alcohol	"	25.9	10.1	62030
13. Chloroform	Acetanilide	18.4	23.2	101800
14. Toluene	Acenaphthene	20.0	25.0	119100
15. Propyl alcohol	"	28.5	18.0	122100
16. Benzene	<i>m</i> -Dinitrobenzene	15.9	22.2	84360

The values of  $\lambda$  have been taken from the International Critical Table, 1928, Vol. V, pp. 151-154).

From the results given above it appears that the value of  $(T_s - T)$  is not constant but varies from 18130 to 122100.

*The relation between  $(T_s - T)$  and  $\sigma V_m$*

In the derivation of the equation

$$\lambda(T_s - T) = 2\sigma V_m \times T_s / r \quad \dots \quad (1)$$

it was assumed that if  $T_s$  remains constant in the case of similar systems then  $(T_s - T)$  must vary directly as  $\sigma V_m$ . If  $\sigma$  and  $V_m$  are known for a particular system, then  $\frac{(T_s - T)\lambda}{\sigma V}$

can be calculated from equation (1). The values so calculated are given Table V.

TABLE V

System.	$\frac{(T_s - T)\lambda}{\sigma V_m}$	$r \times 10^{-6}$ cm.	System.	$\frac{(T_s - T)\lambda}{\sigma V_m}$	$r \times 10^{-6}$ cm.
Benzene—Naphthalene	5.51	2.7	Aniline—Naphthalene	9.69	1.5
Toluene	5.23	2.9	Benzene— <i>m</i> -Dinitrobenzene	12.5	1.2
MeOH	5.09	3.7	Do—Diphenyl	11.3	1.3
CH <sub>3</sub> COOH	6.86	2.2	CHCl <sub>3</sub> --Acetanilide	23.4	0.63

From the results in Table V, it is rather interesting to note that when the solute is the same and the solvent is different, the value  $(T_s - T) \lambda / \sigma V_m$  appears to be constant.

From the results given in Table V, the value of  $r$  has also been calculated from the equation (1), and these values have been calculated for each separate system. (For value of  $r$  see column 3 of Table V). It is very interesting to note that the order of the radius of the stable crystal nucleus is the same as has been determined by other workers.

### *Effect of Heating on the Limits of Supersaturation*

From the results cited in Tables I and II it appears that effect of heating is a general phenomenon as has been observed by other workers. Only a few systems show a small or negligible heating effect.

TABLE VI

	Systems.	$T_s$ .	$S_w$ .	$(T_s - T)_s$ .	$\eta T$ .	$c = S_w/M$ .	$r\phi$
1.	$\text{CCl}_4$ Naphthalene	40°	56.4	3.0	0.01160	0.4375	37.72
2.	$\text{CHCl}_3$ Acenaphthene	35	39.0	15.5	0.01040	0.2533	24.36
3.	Aliline Naphthalene	40	60.0	9.0	0.02461	0.4690	19.05
4.	$\text{C}_6\text{H}_5\text{Br}$ <i>m</i> -Dinitrobenzene	40	61.3	9.0	0.02060	0.2610	12.66
5.	Benzene Naphthalene	40	118.0	6.0	0.00940	0.9220	98.10
6.	$\text{C}_6\text{H}_5\text{Cl}$ „	40	90.0	4.5	0.01045	0.7000	68.70
7.	Toluene „	40	100.0	5.0	0.008459	0.7810	92.32
8.	Hexane „	40	41.1	7.5	0.004255	0.3210	75.47
9.	<i>n</i> -Butyl alcohol „	40	23.0	14.5	0.01880	0.1797	9.56
10.	Acetic acid „	40	28.0	8.5	0.01140	0.2188	19.20
11.	Toluene Acenaphthene	40	47.0	22.0	0.00953	0.3052	30.00
12.	$\text{CH}_3\text{OH}$ „	40	6.0	9.0	0.00506	0.0039	7.70
13.	Benzene <i>p</i> -Dibromobenzene	40	163.0	18.0	0.01130	0.6910	61.00
14.	„ Benzoic acid	40	22.00	8.0	0.00710	0.1803	25.40
15.	$\text{C}_6\text{H}_5\text{NO}_2$ Naphthalene	40	75.0	7.8	0.01670	0.5860	35.10
16.	$\text{CH}_3\text{OH}$ „	35	11.6	4.0	0.005901	0.09060	15.36

Viscosity  $\eta T$  corresponding to the temperature of first spontaneous crystallisation i.e.,  $T$  has been given.

According to Hinshelwood and Hartley (*Phil. Mag.*, 1922, **43**, 78) the heating effect is due to decrease in the catalytic activity of the colloidal dust particles. The concentration of the dust particles present in the beginning will be gradually lowered during the process of heating and shaking. As the concentration of the solute remains constant in a particular experiment, the decrease in the number of dust particles will diminish the number of successful molecular collisions, and thus the value of  $(T_s - T)$  will go on increasing with successive heating and crystallisation or redissolution.

In a previous paper it has been shown that the value of ' $c$ ' where  $c$  is the concentration expressed in g. mols. of solute per 100 g. of solvent and ' $\phi$ ' is the fluidity, to a large extent measures whether there will be any heating effect or not, as fluidity like concentration controls the molecular collisions. It may be expected that the value of ' $c\phi$ ' will control the capacity of forming active centres in a system which leads to crystallisation.

The results of ' $c\phi$ ' values are given in Table VI. The values of ' $c\phi$ ' are taken from the results obtained in this laboratory (this *Journal*, 1948, **25**, 39, 33) where it was not possible to determine viscosity, it has been interpolated from the results. The same temperature of saturation  $T_s$  has been considered in almost all the cases.

The results show that in cases where heating effect is very small or negligible the value of ' $c\phi$ ' is high. Generally in solutions in which ' $c\phi$ ' value is below 30, there is heating effect, but there are few exceptions. These exceptions remain to be explained. We have been regarding the molecules and ions as simple particles of matter, identical in all cases without any specific or individual characteristic of their own. This simple view, though highly helpful in explaining the qualitative properties of solutions, is not applicable to crystal formation from a supersaturated solution. It has been emphasised in previous papers that the attraction between the lattice forming units is necessary for the nucleus formation. If this attraction between the lattice forming units is low, it is possible that no crystalline centres may be formed even though ' $c\phi$ ' values indicate a large probability of molecular impacts. The low mutual affinity among the molecules of organic substances is shown by their easy subliming nature at low temperatures and their low melting points.

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# STUDIES ON THE COMPOSITION OF FERRIC ARSENITE AND FERROUS ARSENATE. PART II. COMPOSITION OF THE SO-CALLED FERRIC ARSENITE (PRODUCT OF MIXING $\text{FeCl}_3$ AND $\text{NaAsO}_2$ )

By ABANI K. BHATTACHARYA

When aqueous solutions of ferric chloride and sodium arsenite are mixed together at high concentrations, a mixture of arsenite and arsenate of iron with some free ferric oxide and adsorbed arsenite is obtained. At low concentration of the reactants, arsenate is completely eliminated, although ferrous iron remains in the compound in appreciable amounts. When aqueous ferric chloride is mixed with neutralised sodium arsenite, the resulting compound retains arsenate in high and low concentrations of the reactants. When aqueous ferric chloride and neutralised sodium arsenite are mixed and the mixture aged for a month, the total quantities of arsenic and iron reach almost a constant limit at all dilutions. When ferric chloride is added more than its equivalent amount to sodium arsenite, a colloidal solution is obtained. When this solution is dialysed for a few weeks, the sample of the product gets completely freed from arsenate and tends to reach a constant composition corresponding to  $\text{Fe}(\text{AsO}_2)_3$ ,  $2\cdot3 \text{ Fe}_2\text{O}_3$ .

In the light of the observations made in Part I of the series of papers (this *Journal*, 1948, 25, 47) quantitative analyses were carried out elaborately in order to throw some light on the composition of iron arsenite and arsenate. In this paper the composition of the product of ferric chloride and sodium arsenite only has been discussed.

## EXPERIMENTAL

The analyses of the products obtained by mixing the reactants under several conditions of concentration, dilution and neutrality were mainly directed to the estimations of  $\text{Fe}^{+++}$ ,  $\text{Fe}^{++}$ ,  $\text{AsO}_2^-$  and  $(\text{AsO}_4)^{-}$  in the compound. The samples were prepared by mixing standard solutions of ferric chloride and sodium arsenite. The precipitates became colloidal on washing, and therefore it was not possible to ensure complete removal of the associated products, by washing over a Bucher funnel. First of all total quantities of iron and arsenic were estimated, then  $\text{Fe}^{+++}$ ,  $\text{Fe}^{++}$ ,  $(\text{AsO}_2^-)$  and  $(\text{AsO}_4)^{-}$  were estimated by the methods detailed below.

*Estimation of total Fe and As.*—A weighed quantity of the sample (0.3 to 0.4 g.) was taken in a beaker and dissolved in a few c. c. of conc. hydrochloric acid (Merck's). The solution was reduced completely by sulphur dioxide so that all arsenate may be reduced to arsenite and ferric to ferrous. Excess of sulphur dioxide was boiled off and then hydrogen sulphide was passed into the solution to precipitate arsenic as  $\text{As}_2\text{S}_3$ . Excess of hydrogen sulphide was removed by bubbling  $\text{CO}_2$ . The precipitated sulphide was filtered in a Gooch crucible, and washed with hot water till free from iron and chloride.  $\text{As}_2\text{S}_3$  was dried at  $105^\circ$  and weighed as usual.

The filtrate was then collected from the filter flask, concentrated by evaporation and estimated as  $\text{Fe}_2\text{O}_3$  after oxidising it with strong  $\text{HNO}_3$ . From this total iron was calculated.

*Estimation of  $\text{Fe}^{+++}$  and  $\text{Fe}^{++}$  in the samples of Ferric Arsenite.*—This was done by matching the intensity of colour by means of a Nephelometer. This instrument was corrected for its zero error. A very dilute solution of ferric chloride, to which a drop of KCNS solution was added, was taken as standard to compare its intensity of colour with that of the ferric arsenite solution of comparable strength in hydrochloric acid. The result was obtained by applying the relation  $M_1/M_2 = h_2/h_1$ , where  $M_1$  and  $M_2$  are the amounts of ferric chloride in the standard  $\text{FeCl}_3$  (M/2490) and in the sample solution, and  $h_1$  and  $h_2$  are the heights of the standard  $\text{FeCl}_3$  and ferric arsenite solution, each coloured with a drop of KCNS solution. Thus the amount  $M_2$  of the ferric iron in the arsenite was obtained,  $M_1$ ,  $h_1$  and  $h_2$  being known. Subtracting the amount of ferric, determined colorimetrically from the total iron already estimated, the quantity of Fe (ous) iron present in the compound was known.

[illegible]

TABLE III

(Sample prepared by ageing)

	Total Fe.	Fe <sup>++</sup>	Fe <sup>+++</sup>	Total Fe.	AsO <sub>2</sub>	AsO <sub>4</sub>	NaCl.
1. <i>M</i> /1.3-Aq. FeCl <sub>3</sub> + <i>M</i> /1.3 neutralised NaAsO <sub>2</sub>	21.13%	16.74%	4.39%	38.55%	49.41%	7.26%	12.18%
	Empirical formula : Fe <sup>+++</sup> <sub>5</sub> -Fe <sup>++</sup> <sub>1.3</sub> -(AsO <sub>2</sub> ) <sub>7.8</sub> (AsO <sub>4</sub> )						
2. <i>M</i> /5-Aq. FeCl <sub>3</sub> + <i>M</i> /5-neutralised NaAsO <sub>2</sub>	20.99	15.24	5.74	40.55	50.51	9.05	10.54
	Empirical formula : Fe <sup>+++</sup> <sub>5</sub> -Fe <sup>++</sup> <sub>1.5</sub> (AsO <sub>2</sub> ) <sub>7.3</sub> (AsO <sub>4</sub> )						
3. <i>M</i> /10-Aq. FeCl <sub>3</sub> + <i>M</i> /10-neutralised NaAsO <sub>2</sub>	21.99	17.44	4.2 1.55	38.96	49.79	7.52	7.31
	Empirical formula : Fe <sup>+++</sup> <sub>5</sub> Fe <sup>++</sup> <sub>1.3</sub> (AsO <sub>2</sub> ) <sub>7.6</sub> (AsO <sub>4</sub> )						

## DISCUSSIONS

The results of the analyses of the samples obtained by mixing FeCl<sub>3</sub> and NaAsO<sub>2</sub> give the following interesting observations :-

(a) When aqueous solutions of ferric chloride and sodium arsenite are mixed together, arsenite and arsenate are formed only in higher concentrations of the reactants (Table I.)

(b) When aqueous solution of ferric chloride is mixed with neutralised solution of sodium arsenite, the resulting compound contains both arsenite and arsenate, at high and low concentrations of the reactants (Table II.).

(c) When aqueous solution of ferric chloride is mixed with neutralised solution of sodium arsenite, and the mixture is allowed to age for a month, the total quantity of iron and arsenite in the samples tends to approach a limit. (Fe, 21.5%, AsO<sub>2</sub>, 50.0%, vide Table III.).

(d) When ferric chloride is added in excess to sodium arsenite, a colloidal solution is formed, which leaves only ferric arsenite on dialysis in the samples, and no excess or free arsenite or arsenate is obtained in the dialysed samples.

(e) Percentage of total iron increases with dilution of the reactants when they are mixed in equivalent proportion (Table I and II). But when the mixed reactants are subjected to ageing, this is not the case. In Tables I and II, it will be further observed that the percentage of total arsenic decreases as the concentration of the reactants is increased, but it does not vary so regularly in the process of ageing or dialysis (Tables III and IV).

Combining all these observations, it can be taken as an established fact that the combination of ferric chloride and sodium arsenite is initiated by mutual oxidation and reduction of the reactants. The ultimate composition of the product depends much on the neutral, acid or alkaline character of the medium. In acidified solutions of ferric chloride, colloidal precipitate is formed which, by dialysis, is reduced to the composition Fe (AsO<sub>2</sub>)<sub>3</sub>, x Fe<sub>2</sub>O<sub>3</sub>.

The analytical results suggest that the composition of the precipitated compound is very much influenced by its hydrolytic and adsorptive properties. Hydrolysis of the compound is supported by the observation that the proportion of iron increases with dilution of the reactants (Tables I and II). The ferric hydroxide formed by hydrolysis remains with the compound, while free arsenious acid is partly washed off into the filtrate in spite of its low solubility. Arsenic acid formed by mutual oxidation and reduction of the reactants or by the hydrolysis of ferric arsenate, is easily washed out, and hence the samples are free from arsenate at higher dilutions. It is well known that ferric hydroxide adsorbs arsenious acid. Bunsen and Berthold ("Das Eisenhydroxyd", 1834) observed that ferric hydroxide had a great power of adsorbing arsenious acid, and considered that basic ferric arsenate was formed. Bitty (*Ber.*, 1904, **37**, 3181) observed that adsorption of arsenious acid by ferric hydroxide follows the well known equation  $x/m/KC^n$ . Hence, there is a great probability of some arsenite remaining adsorbed in the samples of ferric arsenite, the extent of which is difficult to ascertain from the empirical formulae obtained from quantitative analysis, or percentage composition.

Sen (*J. Phys. Chem.*, 1927, **31**, 419) showed that ageing had an appreciable effect on the adsorptive power of ferric hydroxide, and the amount of adsorbed arsenious acid is considerably decreased on ageing. The percentage of arsenious acid in the samples prepared by ageing method is almost constant (Tables III). This may be attributed to the ageing effect on the adsorption of free arsenious acid which may decrease to a constant value for samples prepared under the same conditions and may yield a compound having practically the same composition. The empirical formulae of the samples (Table III) suggest this.

The maximum role of hydrolysis and complete elimination of free arsenious acid and arsenic acid are observed when colloidal solutions of the product are prepared by mixing excess of ferric chloride with aqueous or neutral solution of sodium arsenite, and the mixture is dialysed for several weeks. The composition of the samples leads to a basic compound  $\text{Fe}(\text{AsO}_2)_3 \cdot 2\text{-}3\text{Fe}_2\text{O}_3$  (Table IV).

Although the quantitative estimations of the samples prepared by mixing ferric chloride with aqueous and neutral solutions of sodium arsenite have given a clear evidence of the formation and presence of  $\text{Fe}^{II}$  and  $\text{AsO}_4^{III}$  during the precipitation of the compound, yet it was not possible to determine the exact proportions of ferric arsenite, ferrous arsenate, ferrous arsenite, and ferric arsenate which might have been simultaneously formed. We can, at best, derive an empirical formula. It may further be observed that hydrolysis and adsorption effects which considerably influence the composition of the precipitate, are responsible for the variations in the empirical formulae determined from the analytical results.

Thanks of the author are due to Dr. N. R. Dhar, and Dr. S. Ghosh of Allahabad University, and to Dr. S. S. Deshpande of Agra College, for their keen interest in the investigations.

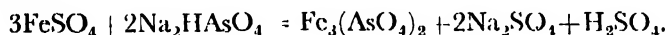


COMPOSITION OF FERRIC ARSENITE AND FERROUS ARSENATE  
PART III. ANALYSIS OF THE SO-CALLED FERROUS ARSENATE  
PRODUCT OF MIXING  $\text{FeSO}_4$  AND  $\text{Na}_2\text{HAsO}_4$

By ABANI K. BHATTACHARYA

Qualitative experiments have shown that mutual oxidation and reduction take place between ferrous sulphate and  $\text{Na}_2\text{HAsO}_4$  only in acid solution. The percentage of arsenite was, however, estimated quantitatively by the method adopted in the analysis of the precipitates obtained by mixing  $\text{FeCl}_3$  with  $\text{NaAsO}_2$  (Part II of the series). From the results of the analysis, the composition of the precipitates obtained by mixing  $\text{FeSO}_4$  and  $\text{Na}_2\text{HAsO}_4$  was found to be more variable with conditions. The composition of the product shows greater similarity when the mixed reactants are allowed to age for several weeks.

To study the composition of the precipitates, qualitative study of the filtrate from samples obtained by mixing the reactants in aqueous, neutral and acidified solutions was made as was done in the case of mixing  $\text{FeCl}_3$  with  $\text{NaAsO}_2$  (this *Journal*, 1948, **25**, 47). It was observed that on mixing aqueous solution of ferrous sulphate and  $\text{Na}_2\text{HAsO}_4$ , a greenish white precipitate was immediately obtained which darkened in colour when left overnight. The precipitate sets to a jelly-like mass. The filtrate is clear and colourless at first but gradually shows a white turbidity; it contains enough ferrous sulphate and is distinctly acidic, showing that the reaction is not quantitative according to the simplest equation



The compound is oxidised on heating and it changes from green to dark brown due to oxidation.

EXPERIMENTAL

Merck's samples of  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  was used and the solution was standardised iodometrically against sodium thiosulphate of known strength. Merck's sample of ferrous sulphate was recrystallised in alcohol and the dried sample was kept in a desiccator. Its solution was standardised against potassium permanganate as usual.

The reactants were then mixed in equivalent proportions and the precipitate was filtered in a Buchner funnel by filter pump, and washed free from sulphate. The precipitate was dried by placing the Buchner funnel over a chimney and in an air-oven at  $100^\circ$ . The dry precipitate was finely powdered in an agate mortar and then subjected to further drying in an air-oven at  $100^\circ$  before transferring to sample tubes.

The samples thus obtained were analysed for  $\text{Fe}^{++}$ ,  $\text{Fe}^{+++}$ ,  $\text{AsO}_4^{--}$  and  $\text{AsO}_3^{--}$  by the same process of analysis as was followed in the case of the precipitate obtained by mixing  $\text{FeCl}_3$  and  $\text{NaAsO}_2$  (vide Part II of the series).



## DISCUSSION

The main points to be observed in the tables are :—

(a) The variations in the total iron content in the samples, prepared under different conditions of acidity and dilution of the reactants, do not exceed 4.40% ; variation of total arsenic is 4.6% only.

(b) The proportions of arsenate and arsenite, and ferric and ferrous change at random.

(c) The composition becomes more similar by the ageing method.

The analytical results can be interpreted on the basis of mutual oxidation and reduction of the reactants. Arsenic acid is stronger than arsenious acid. Hence the arsenate product should suffer less hydrolysis than iron arsenite, and this is supported by simultaneous increase in the proportion of Fe and  $\text{AsO}_4^{''}$ .  $\text{H}_3\text{AsO}_4$  is much more soluble than  $\text{H}_3\text{AsO}_3$  or  $\text{HAsO}_2$ , and hence the proportionate increase of  $(\text{AsO}_4)^{''}$  with increase of Fe suggests that  $\text{H}_3\text{AsO}_4$  is not in the free state but in the form of ferric or ferrous arsenate.

When the iron arsenate is prepared by ageing the mixture of reactants, their mutual oxidation and reduction, and adsorption attain a maximum, and hence the composition becomes more similar. The arsenite formed by mutual oxidation and reduction is slowly oxidised to arsenate on ageing, and therefore the resulting compound contains ferrous, ferric and arsenate components only.

In view of the above observations, it can be concluded that there is a similarity between the mechanism of reaction between a ferric salt and sodium arsenite, and that of a ferrous salt and sodium arsenate. It is not possible, however, to work out their exact molecular formulae by purely analytical methods on account of their hydrolytic and adsorptive properties.

The author owes his thanks to Dr. N. R. Dhar and Dr. S. Ghosh of Allahabad University and to Dr. S. S. Deshpande of Agra College, for their interest in the progress of this piece of investigation.

*Received May 29, 1948.*

## OBITUARY

Mrs. Sheila Dhar

Born : February, 15, 1904.

Died : January 11, 1949.

We are sorry to record the death of Mrs. Sheila Dhar who was a Life-member of the Indian Chemical Society. She was an active member of this Society and a Member of the Council. She did considerable amount of original work in Chemistry. She was born on 15th February, 1905. Her father was late Dr. Paresh Ranjan Roy, a renowned Brahmo leader and the Chief Medical Officer of the Calcutta Corporation. Mrs. Sheila Dhar had her school education in the Diocessan School of Calcutta, and later joined the Central Muir College in 1921 as a first year I.Sc. student. Her laboratory work from the very beginning was highly methodical and accurate. She passed the I.Sc. examination with merit and obtained a scholarship. In the B. Sc. she developed marked capacity for practical work, and obtained a good position securing very high marks in the practical examination. In the M.Sc. examination in 1928 she specialised in Physical Chemistry and obtained a first class first position and presented a thesis on "Influence of Light on Colloids" which has been referred to in many books on colloids and photochemistry. She was awarded a scholarship for research work and carried on important investigations on different aspects of colloids and photochemistry. These have found important mention in text books. She opened a discussion on light absorption and chemical change in the Science Congress in 1933. After her marriage with Dr. N. R. Dhar in 1930, she took great interest in women's welfare work and became a member of various organisations. She accompanied her husband to Europe in 1931 and 1937.

She was gifted with a sweet nature. In spite of her high education, she was most humble and affectionate. She was loved by all who came in contact with her. As she was a staunch follower of Acharya P. C. Ray, she led a noble life of high thinking and simple living. She helped the poor and nursed the sick in a very quiet manner, and never gave publicity to anything that she did.

An end to such a devoted and valuable life is not only a great loss to all her relations and friends but to the women of India and to the Scientific India also, for a woman Scientist of very high reputation is quite rare in this country of ours. May her soul rest in peace.

K. P. C.

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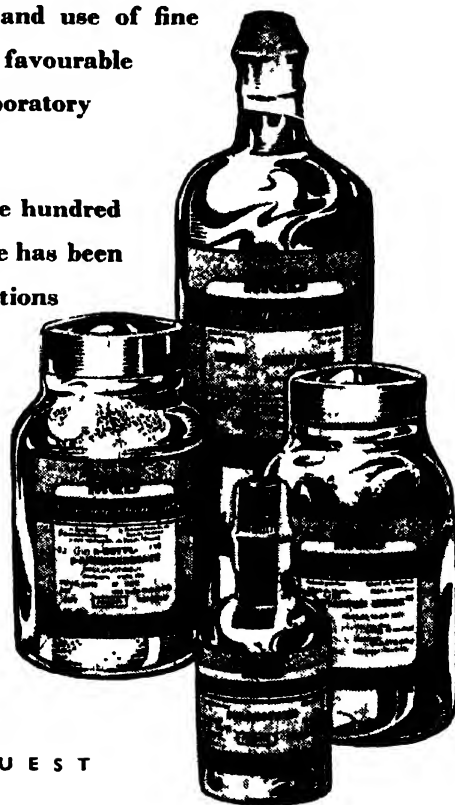
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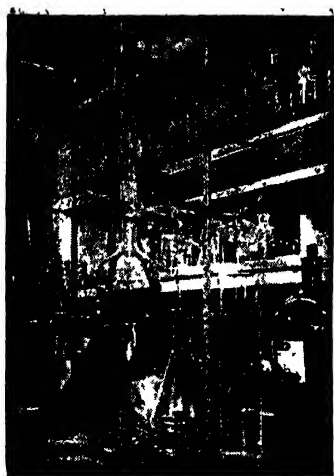
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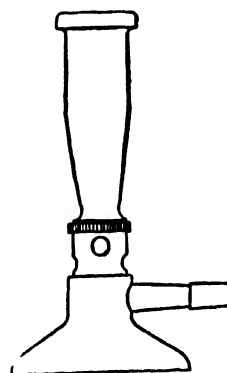
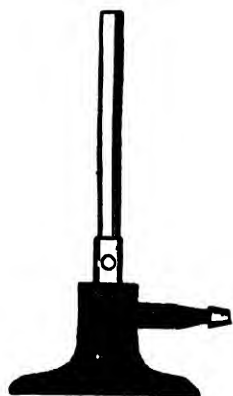
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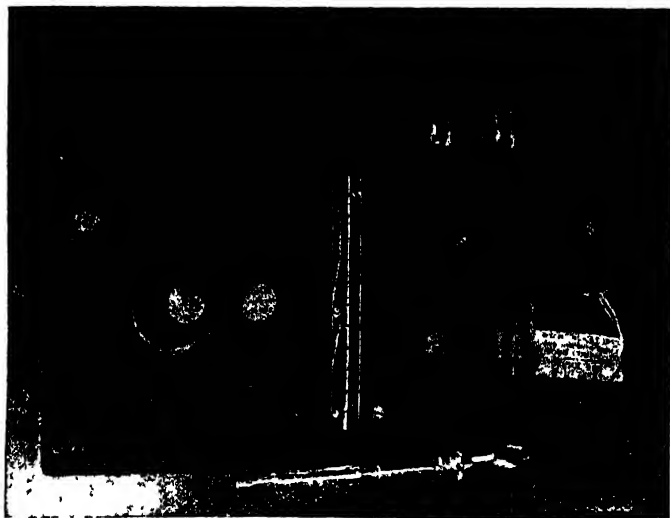
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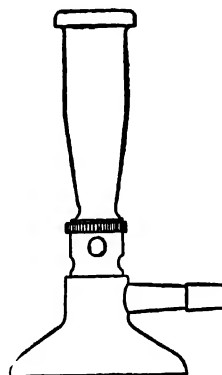
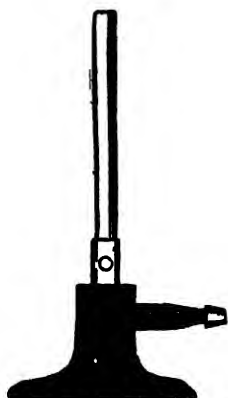
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## DEPENDENCE OF THE OPTICAL ROTATION OF QUININE SALTS ON THE CHARGE OF THE QUININE IONS

BY SUDHAMOY MUKHERJEE

Studies have been made on the variations of the molecular rotations of quinine salts with temperature, concentration and additions of various electrolytes. The rotation increases with dilution and decreases with temperature. The addition of acids to quinine hydrochloride increases its rotation and a maximum value is reached for the addition of 1.47 mols. of hydrochloric acid to each mol. of the quinine salt. Chlorine ions have an inhibiting effect on the rotation of quinine salts and so also have certain other electrolytes which may be placed in the order :  $\text{HCl}$ ,  $\text{NaCl}$ ,  $\text{MgCl}_2 > \text{AlCl}_3 > \text{NaNO}_3 > (\text{COOH})_2 > \text{Na}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4 > \text{Na acetate} (+ \text{H}_2\text{SO}_4) > \text{H}_2\text{SO}_4 > \text{citric acid}$ .

The observations can generally be explained by assuming that the variations are due to variations of the charge on the quinine ions. A quantitative interpretation of the increase of rotatory power of quinine hydrochloride on the addition of hydrochloric acid has been offered on this basis.

The characteristic optical rotatory powers of cinchona alkaloids provide a potentially valuable means for their assay and test of purity, but the sensitiveness of the rotations to various influences often adversely affects the precision of the methods. Since the classical work of Oudemans (*J. Pharm. chim.*, 1884, *v*, **9**, 338), who described a method for the polarimetric estimation of cinchonidine in quinine tartrate, a number of investigators have attempted to develop methods of assay of quinine based on optical rotation. But except for P. Helvetica V and French Codex, 1937, which have adopted optical rotation for limit tests of other alkaloids in quinine, the polarimetric method has not yet come into general usage as a recognised method of assay of quinine alkaloids.

The influence of acids on the rotations of quinine has received considerable attention. Hesse (*Anna'len*, 1873, **166**, 217) first observed that the optical rotation of a quinine salt increased with the addition of acid and a maximum was reached when the amount of acid added sufficed to convert the basic salt into the normal salt. Liquier (*Compt. rend.*, 1926, **183**, 195 ; *Ann. Physique*, 1927, *x*, **8**, 121) found that the curves connecting  $[\alpha]$  with  $p_H$  showed two flat portions corresponding with basic and normal sulphates. Andrews and Webb (*Ind. Eng. Chem., Anal. Ed.*, 1941, **13**, 232) on the other hand failed to confirm the presence of such plateaux in the curve of optical activity corresponding to the two salts. Iapp (*Compt. rend.*, 1933, **196**, 970 ; *Anal. Chim. Appl.*, 1933, **15**, 289) claimed to have observed two inflexions in the  $[\alpha]-p_H$  curves of quinine, one at  $p_H$  4.6 to 6.5 and the other at less than 2.0, corresponding with the basic and neutral salts and suggested a method of the polarimetric estimation of quinine at  $p_H$  5.5. The concentrations of acid in the quinine solution for assay by the optical method, as recommended by different authorities, however, show wide variations and so also the concentrations of quinine and the ratios of acid to quinine present in the solution. This will be apparent from Table I.

TABLE I

Authority.	Quinine salt used.	Acid added.	Conc. of quinine.	Conc. of acid added.	Rotation		Temp.
					$[\alpha]_D$	$[M]_D$	
1. Oudemans ( <i>loc. cit.</i> )	Tartrate (dihydrate)	HCl	0.07425M	0.300N	-221.5°	-882.0°	17°
2. Koppeschaar ( <i>Pharm. J.</i> , 1885, <i>iii</i> , 18, 809)	Tartrate (anhydrous)	HCl	0.0328	0.120	-220.0°	-877.8°	15°
3. French Pharmacopoeia, 1908	Sulphate (anhydrous)	H <sub>2</sub> SO <sub>4</sub>	0.0268	0.0816	-213.5°	-908.3°	15°
4. Allen's Commercial Organic Analysis, Vol. VII, 5th Ed., p. 470	Tartrate, sulphate or hydrochloride	HCl	0.0613	0.225	-272.9° (Q base)	-884.2°	17°
5. French Codex, 1937 (Extra Pharmacopoeia, Martindale, Vol II, 22nd Ed., 1943, p. 143)	Sulphate (anhydrous)	H <sub>2</sub> SO <sub>4</sub>	0.0670	0.0125	-240°	-895.5°	?
6. Thorpe's Dictionary of Applied Chemistry, Vol III, 4th Ed., p. 133	Tartrate (monohydrate)	HCl	0.0613	0.250	-272.9° (Q base)	-884.2°	17°
7. Henry, Plant Alkaloids, 3rd Ed., 1939, p. 399	Sulphate (anhydrous)	H <sub>2</sub> SO <sub>4</sub>	0.025	0.100	-247.1	-921.7°	15°
8. Andrews & Webb ( <i>loc. cit.</i> )	Sulphate (anhydrous)	Nil	0.0077	Nil	-176 (Q base)	-570.3°	25°
9. Do	Bihydrochloride	Nil	0.0077	Nil	-270°	-871.8°	25°

Obviously, if the optical rotation is to be used as a method of assay, standard conditions for the procedure should be established on a rational basis. This would require a study of the various factors on which the rotation depends. Imde (*Helv. Chim. Acta*, 1932, **15**, 557) concluded from his observations that the asymmetric C<sub>9</sub>-atom in the quinine molecule is responsible for a numerically larger amount of rotation than the other three asymmetric carbon atoms put together and that the increase of rotation from the monohydrochloride to the bihydrochloride should be attributed to this C<sub>9</sub>-atom. Again, according to Dietzel and Söllner (*Arch. Pharm.*, 1930, **268**, 629) the increase of rotation of quinine hydrochloride on the addition of acid is due to the ionisation of the quinoline-nitrogen atom. Since the rotation of a dyssymmetric molecule is altered by variations in the dipole forces in the molecule (cf. Kauzmann, Walter and Eyring, *Chem. Rev.*, 1940, **26**, 339), the introduction of a free charge, as by ionisation, should have a marked effect on the rotation. Further, the latter would be influenced by all factors which might cause a variation of this charge. Hydrogen ions would be expected to have a predominant effect on the ionisation of quinine, but the interaction of quinine ions with other ions, by virtue of either chemical or electrical forces, should also modify the effective charge. The ionisation should depend on the concentration and temperature of the solution as well. That such influences do alter the rotation of quinine salts is borne out by the present investigation, details of which are embodied in this paper.

## E X P E R I M E N T A L

*Standard Quinine Solution.*—Quinine sulphate and hydrochloride of B.P. quality, as available in the market, were recrystallised twice from water and dried at 100°. For preparing quinine tartrate, the purified hydrochloride was dissolved in water, and a solution of pure sodium potassium tartrate was added to the boiling solution, which was cooled with continuous stirring. The precipitate of quinine tartrate was recrystallised from water, and finally dried at 100°, *i.e.*, to the monohydrate stage. These salts were used for preparing the standard solutions.

*Polarimetric Measurements.*—A polarimeter by Franz, Smidt and Haenz, reading to 0.01°, in conjunction with an electric sodium lamp was used for the measurements. All readings were taken in a 2 dm. tube. At least 3 readings were taken for each measurement and the mean was taken for calculation of the rotatory power.

The rotatory powers have been expressed in the various tables in terms of both the specific rotation and the molecular rotation, the relationship being

$$[M] = \frac{[\alpha] \times \text{mol. wt.}}{100}$$

For quinine sulphate, which contains two molecules of quinine base, half of the molecular weight was taken for calculation in order to get all the results in terms of the quinine molecule.

*Variations of the Optical Rotatory Power of Quinine Salts with additions of  
Different Electrolytes*

*Quinine Tartrate.*—The salt was dissolved in water with the addition of the minimum quantity of hydrochloric acid to yield a stock solution which was 0.3127*M* with

TABLE II

*Optical rotation of quinine tartrate with additions of electrolytes.*

Conc. of quinine.	Electrolyte added.	Conc. of electrolyte in solution.	$[\alpha]_D^{20}$	$[M]_D^{20}$	Change of rotation due to addition of electrolyte (%).
0.03127 <i>M</i>	None	Nil	-200.2°	-799.0°	...
0.02502	HCl	1.86 <i>N</i>	-182.7°	-729.0°	-8.76 (decrease)
"	NaCl	1.71	$\begin{cases} -179.7^\circ \\ -178.2^\circ \end{cases}$	$\begin{cases} -717.0^\circ \\ -711.0^\circ \end{cases}$	$\begin{cases} -10.26 \\ -11.01 \end{cases}$
"	NaNO <sub>3</sub>	1.18	-190.5°	-760.0°	-4.87
"	$\begin{cases} \text{Na}_2\text{SO}_4 \\ \text{H}_2\text{SO}_4 \end{cases}$	$\begin{cases} 0.70 \\ 0.10 \end{cases}$	-195.1°	-779.6°	-2.43
"	$\begin{cases} \text{Na}_2\text{HPO}_4 \\ \text{HCl} \end{cases}$	$\begin{cases} 2.11 \\ 0.51 \end{cases}$	-196.9°	-785.6°	-1.68
"	H <sub>3</sub> PO <sub>4</sub>	4.01	-197.8°	-789.2°	-1.22
"	CH <sub>3</sub> COOH (glacial)	1.75	-210.9°	-841.5°	+5.32 (increase)

respect to quinine and contained 0.048*N*- hydrochloric acid. The electrolyte was added to 16 c.c. of the solution and the volume in each case was made up to 20 c.c. with water, so that the final concentration of quinine in each case was 0.02502*M*. The results are shown in Table II.

*Quinine Sulphate*.—Quinine sulphate was dissolved in water with the addition of minimum quantity of sulphuric acid. To this stock solution were added electrolytes and water to make up the volume in such proportions that the final solution was in each case 0.0268*M* with respect to quinine and, in most cases, 2.0*N* with respect to the added electrolyte. Besides, the final solution contained 0.0505*N*- sulphuric acid corresponding to the amount added for making the stock solution. The results are given in Table III.

TABLE III

*Optical rotation of quinine sulphate with added electrolytes.*

Quinine=0.0268*M*. H<sub>2</sub>SO<sub>4</sub> (originally present)=0.0505*N*.

No.	Electrolyte added.	Conc. of added electrolyte	$[\alpha]_D^{20}$ .	$[M]_D^{20}$ .	Change of rotation due to electrolyte (%).
1.	None		-23.5°	-833.5°	...
	H <sub>2</sub> SO <sub>4</sub> (N/10) added for dilution	0.0984 <i>N</i>	.		
2.	H <sub>2</sub> SO <sub>4</sub>	2.0	-219.0°	-816.9°	- 2.03
3.	Na <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> added for keeping in soln.	2.0 } 0.2025 }	-215.0°	-802.0°	- 3.79
4.	Na <sub>2</sub> SO <sub>4</sub> HCl added for keeping in soln.	2.0 } 0.0521 }	-214.5°	-800.1°	- 4.02
5.	HCl	2.0	-197.5°	-736.7°	-11.62
6.	NaCl	2.0	-199.5°	-744.1°	-10.74
7.	NaNO <sub>3</sub>	2.0	-211.0°	-787.0°	- 5.59
8.	C <sup>H</sup> <sub>3</sub> COONa H <sub>2</sub> SO <sub>4</sub> added for keeping in soln.	2.0 } 1.53 }	-218.0°	-813.1°	- 2.46
9.	Acetic acid	2.0	-230.0°	-857.9°	+2.55 (increase)
10.	Oxalic acid	2.0	-212.0°	-790.8°	- 5.13
11.	Citric acid	2.0	-219.5°	-818.7°	- 1.79
12.	H <sub>3</sub> PO <sub>4</sub>	6.0	-216.5°	-807.5°	- 3.13
13.	MgCl <sub>2</sub>	2.0	-199.0°	-742.3°	-10.95
14.	AlCl <sub>3</sub>	2.0	-208.5°	-777.7°	- 6.71

Another series of measurements was taken with the same quinine sulphate solution and under identical conditions, but with the addition of varying quantities of sodium chloride. The results are shown in Table IV.

TABLE IV

Conc. of quinine = 0.0268M.

Conc. of NaCl	$[\alpha]_D^{20}$	$[M]_D^{20}$	Change of rotation due to NaCl (%).
0	-223.5°	-833.6°	...
0.0214N	-224.5°	-837.1°	+ 0.45
0.214	-218.0°	-813.1°	- 2.46
0.428	-215.0°	-802.0°	- 3.79
0.856	-209.5°	-781.4°	- 6.26
2.000	-199.5°	-744.1°	-10.74

TABLE V

Optical rotation of quinine hydrochloride with additions of acids.

Conc. of quinine = 0.0322M.

Conc. of acid.	Mol. of acid per equiv. of base	$p_H$	$[\alpha]_D^{20}$	$[M]_D^{20}$	Change of rotation due to acid (%).	$\alpha$	$[M]_{calc}$
1. Nil	1.0	5.80	-151.2°	-545.1°	....	0	-545.1°
2. 0.00526N-HCl	1.1031	5.45	-167.1°	-602.5°	+10.53	0.1635	-598.7°
3. 0.01052	1.3268	4.95	-182.2°	-656.8°	+20.19	0.3280	-652.6°
4. 0.01578	1.4902	1.55	-199.4°	-734.5°	+32.91	0.4888	-705.2°
5. 0.02104	1.6536	4.25	-212.3°	-765.5°	+40.43	0.6509	-758.3°
6. 0.02630	1.8170	3.95	-225.2°	-812.1°	+49.17	0.8110	-810.8°
7. 0.03156	1.9804	3.70	-236.0°	-850.6°	+56.01	0.9530	-857.3°
8. 0.03682	2.1438	3.12	-240.3°	-866.5°	+58.98		
9. 0.04734	2.4706	2.85	-243.0°	-872.7°	+60.10		
					Diff. from maximum value.		
10. 0.1053	4.268	1.75	-237.7°	-857.1°	- 1.79		
11. 0.1579	5.907	1.58	-233.9°	-843.2°	- 3.38		
12. 0.2752	9.547	Not detd.	-232.6°	-838.5°	- 3.92		
13. 1.2384	39.46	"	-217.5°	-784.2°	-10.24		
14. 1.9500	61.56	"	-208.4°	-751.5°	-13.89		
					Diff. from orig. rotation.		
15. 0.03156N-H <sub>2</sub> SO <sub>4</sub>	1.9804	"	-236.4°	-852.5°	+56.40		
16. 0.04734	2.4706	"	-241.2°	-870.0°	+59.60		

*Quinine Hydrochloride.*—Varying quantities of standard hydrochloric acid and sulphuric acid solutions were added to a given volume of a solution of quinine hydrochloride in water, keeping the final volume constant in each case by the addition of water. The final concentration of quinine was in each case 0.0322M. The variations of the  $p_H$  values and of the optical rotations are given in Table V.

A similar study was made of the influence of varying concentrations of sodium chloride on the optical rotation of quinine hydrochloride, with or without the previous addition of hydrochloric acid in proportion sufficient to raise the rotation to the maximum value. The results are shown in Table VI.

TABLE VI

*Optical rotation of quinine hydrochloride with addition of HCl and/or NaCl.*  
Conc. of quinine = 0.0322M.

No.	Concentration. HCl.	NaCl.	[C]	$[\alpha]_D^{20}$ .	$[M]_D^{20}$ .	Change of rotation due to electrolyte (%).
1.	Nil	Nil	0.0322N	-151.2°	-545.1°	...
2.	"	0.0577N	0.0899	-150.7°	-543.5°	-0.29
3.	"	0.2885	0.3207	-149.9°	-540.4°	-0.86
4.	"	0.5770	0.6092	-147.6°	-535.7°	-1.72
5.	"	1.2384	1.2706	-143.5°	-518.6°	-4.86
						Diff. from maximum value.
6.	0.0511N	0.0577	0.1410	-138.6°	-860.2°	-1.43
7.	0.0511	1.1870	1.2713	-117.5°	-781.2°	-10.14

*Variations of Optical Rotation of Quinine Salts with Temperature*

The rotation of a 0.06805M solution of quinine tartrate containing 0.24N sulphuric acid was determined at temperatures 25°, 30° and 35°. Similar measurements were made with a 0.053M solution of quinine sulphate in 0.0969 N-sulphuric acid at temperatures 30.6°, 37.4° and 51.2°, and in this case the refractive indices of the solutions were also determined at the corresponding temperatures using a Zeiss dipping refractometer. The results are shown in Table VII.

TABLE VII

*Variations of optical rotation of quinine salts with temperature*

Temp.	$[\alpha]_D$ .	$[M]_D$ .	Ref. index.	$\left(\frac{n^2+2}{3}\right)^2$	$\frac{[M]_D}{\left(\frac{n^2+2}{3}\right)^2}$
Quinine tartrate (0.06805 M)					
25°	-216.2°	-862.6°	...	...	...
30°	-209.4°	-835.5°	...	...	...
35°	-201.3°	-803.2°	...	...	...
Quinine sulphate (0.0969 M)					
30.6°	-221.9°	-827.7°	1.33700	1.50396	-519.3
37.4°	-218.1°	-813.5°	1.33602	1.50172	-511.1
51.2°	-211.8°	-790.0°	1.33372	1.58659	-498.0

*Variations of the Optical Rotation with Concentration of Quinine Salts*

A few measurements were taken for studying the effect of concentration on the optical rotations of quinine tartrate and hydrochloride solutions. The results are shown in Table VIII.

TABLE VIII

*Optical rotations of quinine salts at varying concentrations.*

No.	Particulars.	Conc. of quinine	$[\alpha]_D^{20}$	$[M]_D^{20}$
1.	Quinine tartrate (in 0.48N-HCl)	0.31270 M	-191.1°	-762.5
2.	Do diluted 10 times	0.03127	-201.0°	-802.1
3.	Quinine tartrate (in 0.24N-H <sub>2</sub> SO <sub>4</sub> )	0.06805	-209.4°	-835.5°
4.	Do diluted with equal volume of water	0.03402	-214.7°	-856.7°
5.	Quinine hydrochloride (in aq. soln.)	0.06120	-148.7°	-536.0°
6.	Do 10 c.c. diluted to 19 c.c. with water	0.03220	-151.2°	-545.1°

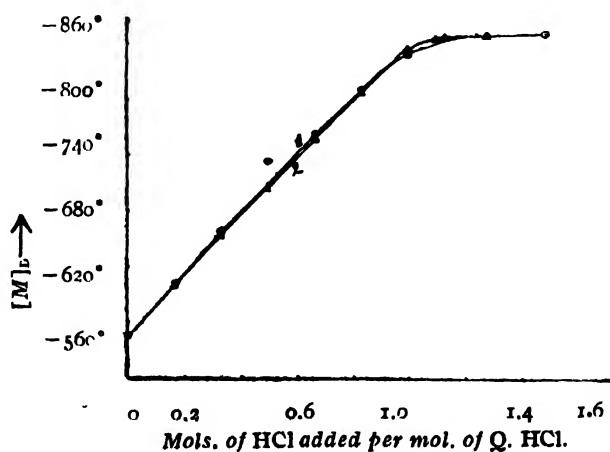
## DISCUSSION

The results recorded above show that the molecular rotations of different quinine salts at similar concentrations are not identical, though the variations are not large. The following order has been noticed:

Q.HCl (in excess HCl) > Q<sub>2</sub> H<sub>2</sub>SO<sub>4</sub> (in excess H<sub>2</sub>SO<sub>4</sub>) > Q tartrate (in excess HCl) > Q.HCl (aqueous solution).

It seems that caution is necessary in accepting the sweeping generalisations sometimes made, e.g., that all quinine salts, containing an equivalent amount of alkaloid, give the same rotation when dissolved in the same large excess of hydrochloric acid (Allen's Commercial Organic Analysis, Vol. VII, 5th Ed., p. 470).

FIG. 1

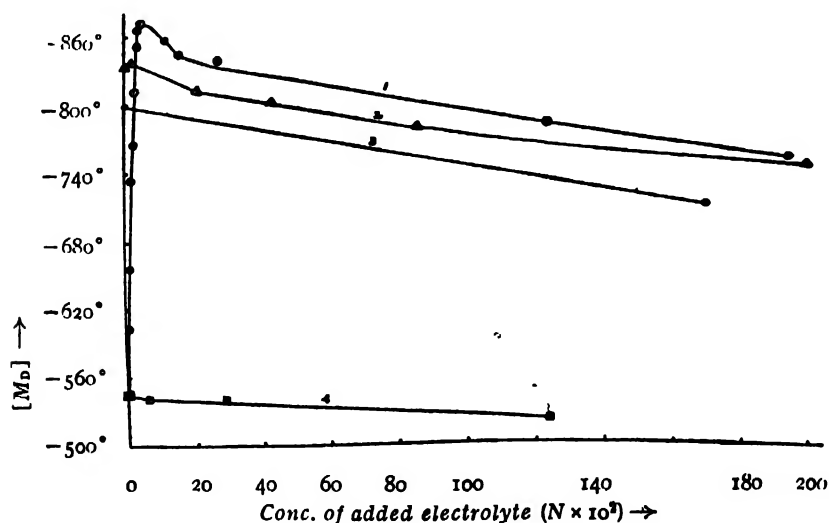


Among the electrolytes studied, acids have the greatest effect on the optical rotation of quinine. Curve 1 in Fig. 1 shows that the rotation of quinine hydrochloride increases almost linearly with additions of hydrochloric acid till about 0.9 equivalent of acid has been added to one molecule of quinine. The curve bends subsequently and a maximum rotation is reached for the addition of 1.47 equivalents of acid. This observation is in consonance with those of Dietzel and Sollner (*loc. cit.*) but is at variance with the statements often made that the maximum rotation corresponds with the formation of the bihydrochloride of quinine, *i.e.*, with the addition of one equivalent of acid per molecule of quinine (cf. Thorpe's Dictionary of Applied Chemistry, 4th Ed., Vol. III, p. 149; Liquier, *loc. cit.*).

An exactly similar increase of rotation of the quinine hydrochloride solution takes place on the addition of sulphuric acid in place of hydrochloric acid, at the corresponding concentrations (vide Table V). This indicates that the effect is due to hydrogen ions of the acid.

Fig. 2, curve 1 shows that after the maximum rotation of the quinine hydrochloride solution has been reached, further addition of hydrochloric acid causes a gradual decrease of the rotation and that this decrease from the maximum value amounts to about 14% as the concentration of the acid approaches 2.0 *N* (vide Table V). If again after sufficient hydrochloric acid has been added to the quinine hydrochloride for attaining the maximum rotation, sodium chloride is added instead of hydrochloric acid, the rotation is decreased to exactly the same extents as with the additions of corresponding equivalent quantities of the acid (vide Table VI, also Fig. 2). This shows that the decrease of rotation is in both cases due to the increase of chlorine-ion concentration. [The decrease of rotation due to the addition of excess hydrochloric acid was noticed by Hesse (*loc. cit.*)

FIG. 2



Curves 1—4 refer respectively to  $Q.HCl + HCl$ ;  $Q_2.H_2SO_4 + NaCl$ ;  $Q.tartrate + NaCl$ ,  $Q.HCl + NaCl$ ; + sign refers to  $Q.HCl + 0.0511N-HCl + NaCl$ .



but no further reference to any investigation of this point was found in the literature].

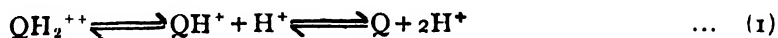
That chlorine ions have a depressing effect on the rotations of other quinine salts as well is shown by curves 2, 3 and 4 in Fig. 2, corresponding to quinine sulphate, tartrate and hydrochloride respectively (cf. also Tables II, III, IV and VI). With quinine sulphate (Table III), the addition of hydrochloric acid, sodium chloride and magnesium chloride had nearly the same effect at 2*N* concentration, but the lowering of rotation caused by aluminium chloride was appreciably smaller. It appears that the cation has little effect on the rotation and the smaller effect of the aluminium salt is presumably due to a lower activity of the chlorine ions in aluminium chloride solution.

Tables II and III show the effect of several other electrolytes on the rotations of quinine tartrate and sulphate respectively. It will be seen that although most of the electrolytes added have a lowering effect on the rotation in a greater or less degree, chlorides have by far the maximum effect. These may be arranged in the following order:  $\text{HCl}$ ,  $\text{NaCl}$ ,  $\text{MgCl}_2 > \text{AlCl}_3 > \text{NaNO}_3 > (\text{COOH})_2 > \text{Na}_2\text{SO}_4 > \text{H}_3\text{PO}_4 > \text{Na-acetate}$  ( $+ \text{H}_2\text{SO}_4$ )  $> \text{H}_2\text{SO}_4 > \text{citric acid}$ .

The observations indicate that the effects are probably due to the anions, but the above order does not strictly correspond to the order of valency, though the monovalent chlorine and nitrate ions show the largest effect and the tribasic citric acid, the minimum effect. Acetic acid provides an exception by increasing the rotations of both the quinine salts studied, but sodium acetate causes a small decrease. This point deserves further investigation.

Since the electrolytic ions probably exert their influence on the rotation of quinine salts, the rotatory power of quinine would also appear to depend on the ionic form in which it is present. Quinine being a diacidic base may exist in solution in the following forms:  $\text{Q}$ ,  $\text{QH}^+$  and  $\text{QH}_2^{++}$ .  $\text{QH}^+$  should be present mainly in the hydrochloride solution and  $\text{QH}_2^{++}$  in the bishydrochloride, and so a difference in the optical rotatory powers of the two ionic forms would qualitatively explain the nature of the variations observed on the addition of acid to the hydrochloride. Hypotheses on such basis have previously been postulated by Liquier (*loc. cit.*), Lapp (*loc. cit.*) and by Dietzel and Söllner (*loc. cit.*).

A quantitative examination of the question would involve the calculation of the proportions of the two types of ions at various stages during the addition of acid to quinine hydrochloride. In a mixture of quinine hydrochloride and hydrochloric acid, the following equilibrium may be assumed to exist:



The values of the dissociation constants  $K_1$  and  $K_2$  of the  $\text{QH}_2^{++}$  ion are  $4.3 \times 10^{-5}$  and  $2 \times 10^{-11}$  respectively (Pedersen, *Dansk. Tids. Farm.*, 1934, 8, 17). On account of the large difference between the values of the two dissociation constants, the second stage of dissociation, i.e., the concentration of the uncharged  $\text{Q}$  molecules, may be

neglected in an acidic solution, as obtains during the addition of acid to quinine hydrochloride. The equation for electroneutrality in such a solution may be written as:

$$\frac{[\text{QH}_2^{++}]}{Cx} + \frac{[\text{QH}^+]}{C(1-x)} + \frac{[\text{H}^+]}{(C_1 - Cx)} = \frac{[\text{Cl}^-]}{(C + C_1)} \quad \dots (2)$$

where  $C$  is the molar concentration of quinine,  $C_1$ , the concentration of added hydrochloric acid and  $x$  is the fraction of the quinine molecules present in the  $\text{QH}_2^{++}$  form. Therefore,

$$K_1 = \frac{[\text{QH}^+][\text{H}^+]}{[\text{QH}_2^{++}]} = \frac{C(1-x)(C_1 - Cx)}{Cx}, \text{ whence,}$$

$$Cx^2 - x(C + C_1 + K_1) + C_1 = 0 \quad \dots (3)$$

The values of  $x$  calculated from the quadratic equation (3) with different values of  $C_1$ , are given in column 8 of Table V.

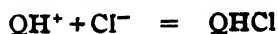
If we now assume the value  $-545.1^\circ$  for the molecular rotation of quinine hydrochloride as due to  $\text{QH}^+$  ions alone, and the maximum value  $-872.7^\circ$  as due solely to  $\text{QH}_2^{++}$  ions, the molecular rotation of a solution containing a mixture of the two ionic forms will be given by

$$[M]_{\text{calc}} = -(545.1^\circ + 327.6 \lambda) \quad \dots (4)$$

The values of  $[M]_{\text{calc}}$ , calculated from equation (4) are given in the last column of Table V. Curve 2 in Fig. 1 was obtained by plotting the above values, but the last three points represent the values of  $[M]_{\text{calc}}$  corresponding to those of  $C_1$  calculated from equation (3) by substituting respectively the values 0.985, 0.99 and 0.995 for  $x$ . The close correspondence between the observed and calculated curves tends to justify the assumptions on which the calculations were made.

Since the optical rotatory power of quinine shows increase with the charge of the quinine ions, factors which would alter the charge would be expected to alter the rotation also. When chlorine ions are added in excess to quinine hydrochloride in acid solution having the maximum rotation, an association of the oppositely charged ions,  $\text{QH}_2^{++}$  and  $\text{Cl}^-$  to form a complex of the type  $\text{QH}_2\text{Cl}^+$  might be considered as taking place. This would reduce the effective charge of the quinine ion, and therefore the rotation, as observed in curves 1, 2 and 3 in Fig. 2. The slopes of the descending portions of these three curves are almost identical, tending to indicate that the same type of interaction is taking place in these cases.

Curve 4 in Fig. 2 for quinine hydrochloride and sodium chloride shows a slower decrease of rotation with increase of chlorine ions. Here, an ion-association of the type



may be postulated, but the attractive force would be weaker than that between  $\text{QH}_2^{++}$  and  $\text{Cl}^-$ , which would explain the smaller depression of the optical rotation.

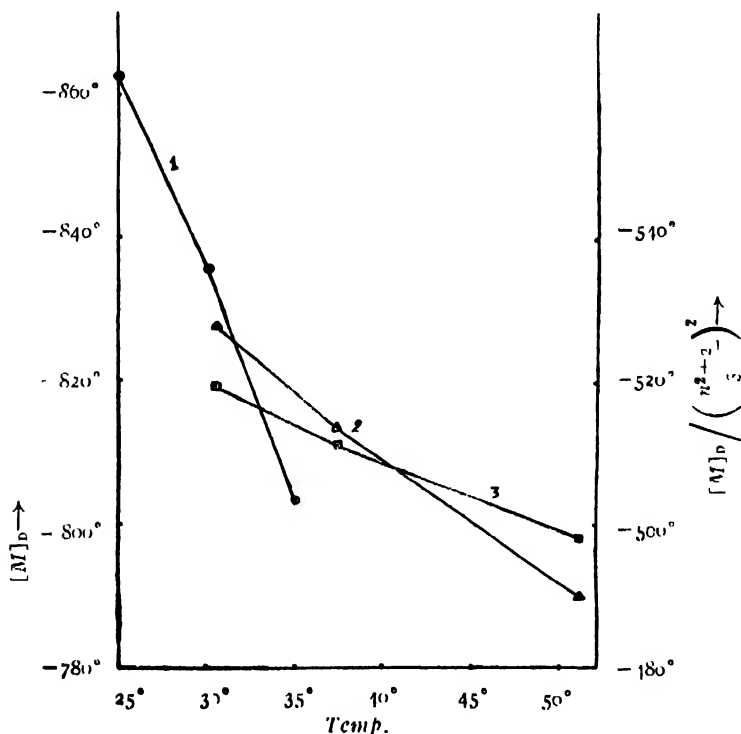
Similarly, the effect of other electrolytes in reducing the optical rotation of quinine salts may be attributed to the interaction between the quinine cations and the anions of the electrolytes to form ion-complexes of reduced charge. A regular variation of the effect with the valency of the added anion would be expected in such cases, but the observed absence of such regularity, the characteristically prominent effect of chlorine ions and the anomalous behaviour of acetic acid point to some sort of specificity in these interactions.

Table VIII shows that a decrease of the concentration of quinine salts results in an increase of the molecular rotation. This would appear to be due to the dissociation of the salt molecules into the respective ions resulting in an increase of the ionic forms which produce higher rotations.

The rotation of quinine salts is found to decrease with increase of temperature (vide Table VII and Fig. 3). Increase of temperature may bring about, among others, the following types of changes in the solution of the quinine salt :—

- (1) Decrease of density resulting in a decrease of the refractive index.
- (2) Increase of the freedom of rotation within the molecules, thus reducing the asymmetry (e.g., about the axis joining the  $C_8$  and  $C_9$  carbon atoms).

FIG. 3



According to Guye and Aston (*Compt. rend.*, 1897, 124, 194; also cf. Walden, *Ber.*, 1905, 38, 363), optical rotation generally decreases with increasing temperature, but

the magnitude of the decrease is usually rather small and probably results from decrease in refractive index due to decrease in density. This conclusion would, however, apply to molecules already possessing freedom of rotation. The following relations have been found to hold between the refractive index,  $n$ , and molecular rotation (Kauzmann, Walter and Eyring, *loc cit.*)

$$[M]_D \div \left( \frac{n^2 + 2}{3} \right) = \text{Constant} \quad \dots (5)$$

$$[M]_D + \left( \frac{n^2 + 2}{3} \right)^2 = \text{Constant} \quad \dots (6)$$

Equation (6) is said to have given better constancy in certain cases. The values of  $[M] / \left( \frac{n^2 + 2}{3} \right)^2$ , calculated for quinine sulphate, have been given in the last column of Table VII and also plotted in curve 3, Fig. 3.

Comparison of the curves 2 and 3 in Fig. 3 shows that although the slope of the change is reduced by correcting the molecular rotation for refractive index in the above manner, actual constancy is not thereby attained. This would indicate that other factors also come into play including the increase of freedom of rotation of the molecule about the axis connecting the asymmetric carbon atoms  $C_\alpha$  and  $C_\beta$ .

Further work on the standardisation of conditions for the assay of quinine by optical rotation is in progress.

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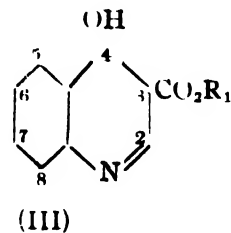
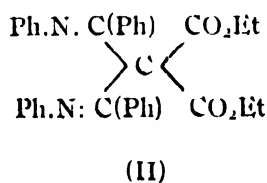
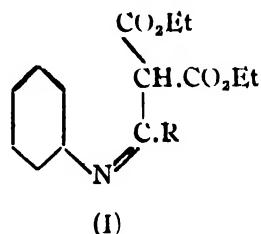
# IMIDOCHLORIDES. PART VIII. REACTION OF ANILIDE IMIDOCHLORIDES WITH ETHYL SODIOMALONATE. SYNTHESIS OF SOME 4-HYDROXY-2-ARYL-3-CARBETHOXYQUINOLINES

K. D. KULKARNI AND R. C. SHAH

In extension of the previous work of Shah and Heeramanek (*J. Chem. Soc.*, 1936, 428, 1937, 867) ethyl sodiomalonate has been condensed with various anilide imidochlorides containing substituents in the acid part of the molecule. The crude condensation products have been cyclised by heating under reduced pressure to the corresponding 4-hydroxy-2-aryl-3-carbethoxyquinolines, and the latter then hydrolysed to the corresponding carboxylic acids.

Just condensed equimolecular proportions of benzanilide imidochloride with ethyl sodiomalonate in ether and isolated (i) mono- $\alpha$ -phenyliminobenzylmalonic acid diethyl ester (I, R=Ph) and (ii) di- $\alpha$ -phenyliminobenzylmalonic acid diethyl ester (II). He also observed that the mono-condensation product (I, R=Ph) underwent cyclisation on heating at higher temperatures affording 4-hydroxy-2-phenyl-3-carbethoxyquinoline (III, R=Ph; R<sub>1</sub>=H). He extended the above reaction to benz-*o*- and -*p*-toluidide imidochlorides and  $\alpha$ - and  $\beta$ -naphthalide imidochlorides (Just, *Ber.*, 1885, 18, 2623; 1886, 19, 983, 1462, 1541).

Shah and Heeramanek modified the above method by carrying out the condensation in dry toluene and employing one additional mole of free ethyl malonate, thereby minimising the formation of the di-condensation product and improving the yield of the mono-condensation product and consequently that of the quinoline. They have applied the above modified method to the condensation of various substituted anilide imidochlorides and also to the imidochlorides derived from benzoyl derivatives of  $\alpha$ - and  $\beta$ -naphthylamines, and have shown this synthesis to be of general applicability (Shah and Heeramanek, *J. Chem. Soc.*, 1936, 428; 1937, 867). Elderfield and co-workers have also applied this modified method for the synthesis of some substituted 4-hydroxy-2-phenylquinolines from the corresponding imidochlorides (*J. Amer. Chem. Soc.*, 1946, 68, 1272).



In extension of the work of Shah and Heeramanek (*loc. cit.*) ethyl sodiomalonate has been successfully condensed with anilide imidochlorides substituted in the acid part of the molecule. The imidochlorides employed in the present investigation were derived from *o*-, *m*- and *p*-toluic acids, *m*- and *p*-bromobenzoic acids, *p*-methoxybenzoic acid and  $\beta$ -naphthoic acid.

Except in the case of  $\beta$ -naphthanilide imidochloride, the intermediate condensation products could not be crystallised and the crude products were directly cyclised when 4-hydroxy-2-aryl-3-carbethoxyquinolines (III, R=aryl; R<sub>1</sub>=Et) with various substituents in the 2-phenyl ring were obtained, which are new. The condensation of  $\beta$ -naphthanilide imidochloride with ethyl sodiomalonate afforded crystallisable intermediate condensation product, which on cyclisation gave 4-hydroxy-2- $\beta$ -naphthyl-3-carbethoxyquinoline (III, R= $\beta$ -naphthyl; R<sub>1</sub>=Et). All the 3-carbethoxyquinolines, obtained as above, on hydrolysis gave the corresponding quinoline-3-carboxylic acids (III, R=aryl; R<sub>1</sub>=H).

The results of the present work have further shown the general applicability of the synthesis and that the presence of substituents in the acid part of the imidochloride molecule does not seem to appreciably effect either its condensation with ethyl sodiomalonate or the cyclisation of the condensation product to the quinoline derivative.

Shah and Heeramanek (*loc. cit.*) carried out the cyclisation of the intermediate condensation products by heating them above 180° (under atmospheric pressure), but in the present work it has been observed that the same could be effected more smoothly by treating them at 160°-170° under reduced pressure.

#### EXPERIMENTAL

Anilides required for the purpose were prepared by the method recommended by Shah and Deshpande (*J. Univ. Bombay*, 1933, 2, II, 126).

*o*-Toluanilide imidochloride was prepared by heating *o*-toluanilide (10 g.) and phosphorus pentachloride (14 g.) till the evolution of fumes of hydrochloric acid ceased. It distilled at 160°-170°/10 mm., m.p. 36°, yield 5 g. (Found: Cl, 14.9. C<sub>11</sub>H<sub>7</sub>NC1 requires Cl, 15.5 per cent).

*Condensation of o-Toluanilide Imidochloride with Ethyl Sodiomalonate: 4-Hydroxy-2-o-tolyl-3-carbethoxyquinoline.*—*o*-Toluanilide imidochloride (5 g., 1 mol.) was refluxed with ethyl sodiomalonate, prepared from ethyl malonate (10 g., 2 mol.) and sodium (0.6 g., 1 atom), in dry toluene at 130°-140° for 2 hours. The cooled reaction mixture was then treated with water and extracted with ether. Ether was distilled out under atmospheric pressure, and the toluene and excess of ethyl malonate were removed under reduced pressure. The crude condensation product so obtained could not be crystallised and was heated for cyclisation at 150°-160° under reduced pressure till the evolution of bubbles of ethyl alcohol ceased. The reaction mixture was then treated with cold alcohol when the quinoline derivative was obtained in crystalline form. It was recrystallised from hot alcohol, m.p. 184-86°, yield 2 g. (Found: N, 4.1. C<sub>19</sub>H<sub>17</sub>O<sub>3</sub>N requires N, 4.6 per cent).

*4-Hydroxy-2-o-tolylquinoline-3-carboxylic Acid.*—The ethyl ester obtained as above was hydrolysed by refluxing with alcoholic sodium hydroxide for 2 hours. The acid obtained on acidification with hydrochloric acid was crystallised from acetic acid, m.p. 198°-200° (decomp.). (Found: N, 4.5. C<sub>17</sub>H<sub>13</sub>O<sub>3</sub>N requires N, 5.0 per cent).

The following compounds were prepared by the method described above. All the esters were crystallised from alcohol, whereas the corresponding acids were crystallised from acetic acid unless otherwise mentioned. The percentage yields of the quinolines are calculated on the weight of the imidochlorides employed.

*m*-Toluanilide imidochloride, prepared from *m*-toluanilide (10 g.) and phosphorus pentachloride (14 g.), distilled at 210°-220°/33 mm., m.p. 37°. (Found: Cl, 15.0.  $C_{14}H_{12}NCl$  requires Cl, 15.5 per cent).

4-Hydroxy-2-*m*-tolyl-3-carbethoxyquinoline was obtained from *m*-toluanilide imidochloride, m.p. 175-77°, yield 19%. (Found: N, 4.5.  $C_{17}H_{15}O_3N$  requires N, 4.6 per cent).

4-Hydroxy-2-*m*-tolylquinoline-3-carboxylic acid, m.p. 183-86° (decomp.). (Found: N, 4.9.  $C_{17}H_{13}O_3N$  requires N, 5.0 per cent).

*p*-Toluanilide imidochloride was prepared from *p*-toluanilide (14 g.) and phosphorus pentachloride (10 g.), yield 10 g. It distilled at 200°/16 mm. and had m.p. 45°. (Found: Cl, 15.2.  $C_{11}H_{12}NCl$  requires Cl, 15.5 per cent).

4-Hydroxy-2-*p*-tolyl-3-carbethoxyquinoline was prepared from *p*-toluanilide imidochloride, yield 9%, m.p. 233-35° (Found: N, 4.0.  $C_{17}H_{15}O_3N$  requires N, 4.6 per cent).

4-Hydroxy-2-*p*-tolylquinoline-3-carboxylic acid, m.p. 273-75° (decomp.). (Found: N, 4.5.  $C_{17}H_{13}O_3N$  requires N, 5.0 per cent).

*m*-Bromobenzanilide imidochloride was prepared from *m*-bromobenzanilide (14 g.) and phosphorus pentachloride (14 g.), b.p. 230-240°/50 mm., m.p. 39°. (Found: Halogen, 39.0.  $C_{13}H_9NClBr$  requires halogen, 39.2 per cent).

4-Hydroxy-2-*m*-bromophenyl-3-carbethoxyquinoline was prepared from *m*-bromobenzanilide imidochloride, m.p. 231-33°. (Found: Br, 20.7.  $C_{17}H_{14}O_3NBr$  requires Br, 21.5 per cent).

3-Hydroxy-2-*m*-bromophenylquinoline-3-carboxylic acid, m.p. 238°-40° (decomp.). (Found: Br, 22.9.  $C_{18}H_{10}O_3NBr$  requires Br, 23.2 per cent).

*p*-Bromobenzanilide imidochloride was prepared by Shah and Chaubal's method (*J. Chem. Soc.*, 1932, 652), m.p. 85-86°. Wheeler and Johnson (*Amer. Chem. J.*, 1903, **30**, 24,) give m.p. 78°.

4-Hydroxy-2-*p*-bromophenyl-3-carbethoxyquinoline from *p*-bromobenzanilide imidochloride (yield 24%), m.p. 258-60°. (Found: Br, 21.1.  $C_{18}H_{11}O_3NBr$  requires Br, 21.5 per cent).

4-Hydroxy-2-*p*-bromophenylquinoline-3-carboxylic acid, m.p. 277°-80° (decomp.). (Found: Br, 22.5.  $C_{18}H_{10}O_3NBr$  requires Br, 23.2 per cent).

*p*-Methoxybenzanilide imidochloride distilled at 212°/11 mm. (Found: Cl, 13.9. Calc. for  $C_{14}H_{13}ONCl$ : Cl, 14.4 per cent). Wheeler and Johnson (*loc. cit.*) give m.p. 70°.

4-Hydroxy-2-p-methoxyphenyl-3-carbethoxyquinoline was prepared from p-methoxybenzanilide imidochloride, yield 28%, m.p. 216-20°. (Found: N, 4.0.  $C_{19}H_{17}O_4N$  requires N, 4.3 per cent).

4-Hydroxy-2-p-methoxyphenylquinoline-3-carboxylic acid, m.p. 226°-29° (decomp.). (Found: N, 4.0.  $C_{17}H_{15}O_4N$  requires N, 4.7 per cent).

$\alpha$ -[Phenylimino-( $\beta$ -naphthylmethyl)] malonic Acid Diethyl Ester.—The condensation of  $\beta$ -naphthanilide imidochloride (Shah and Chaubal, *loc. cit.*) and ethyl sodiomalonnate afforded the above as a pasty mass after usual treatment. It was left in a frigidaire for few days after which it solidified to a whitish mass. It was washed with petroleum ether, and after crystallisation from alcohol it gave a white solid, m.p. 150-52° (Found: N, 3.9.  $C_{24}H_{23}O_4N$  requires N, 3.6 per cent).

4-Hydroxy-2- $\beta$ -naphthyl-3-carbethoxyquinoline was prepared from the above, m.p. 227-30°. (Found: N, 3.6.  $C_{22}H_{17}O_3N$  requires N, 4.1 per cent).

4-Hydroxy-2- $\beta$ -naphthylquinoline-3-carboxylic acid, m. p. 238-40° (decomp.). (Found: N, 4.1.  $C_{20}H_{15}O_3N$  requires N, 4.4 per cent).

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## ERRATA

In part VII of the paper published in the March issue of this Journal (1949) please

Page	Line	read in	
122	19	(III)	for (II)
123	1	$C_{18}H_{15}O_2N$	,, $C_{18}N_{15}O_2N$



## SYNTHESIS OF SOME NEW ACRIDINE DERIVATIVES. PART I

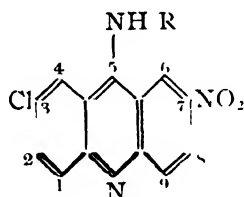
BY KUNDAN SINGH AND BASHIR AHMAD

Certain dialkylamino-alkylamino-acridines, substituted phenylamino-acridines, sulphanilamido-acridines and acetylaminobenzene sulphonamido acridines have been synthesised for studying their antimalarial and antiseptic properties.

Acridine derivatives, like atehrin and acriquine, which contain a dialkylamino-alkylamino chain at position 5, possess strong antimalarial properties (Kikuth, *Deut. Med. Wchschr.*, 1932, **58**, 530; Magidson and Grigorowsky, *Ber.*, 1936, **69B**, 396; Mietsch and Mauss, *Klin. Wchschr.*, 1933, **12**, 1276; Magidson and Grigorowsky, *Khm. Farm. Prom.*, 1935, No 1, 26-34). Magidson and Grigorowsky (*loc. cit.*) have noticed that the antimalarial chemotherapeutic index of 8-nitro derivatives is increased if the nitro group is transferred from 8 to 7 position in the acridine molecule. Further, the acridines, which are substituted by a halogen atom in any particular position, show antimalarial properties (Mietsch and Mauss, *loc. cit.*).

5-Aminoacridines, which contain a nitro or amino group, have been shown to possess good antiseptic properties (Schnitzar and Silberstein, *Z. Hyg. Infek.*, 1920, **109**, 519; Albert *et al.*, *Brit. J. Exptl. Path.*, 1938, **19**, 41).

In view of the above facts it was thought desirable to prepare compounds of the general formula



where-NHR represents different straight chained dialkylamino-alkylamino, substituted phenylamino, sulphanilamide, amino, and *p*-acetylaminobenzene sulphonylamino groups. The nitro group was further reduced to amino group and the latter acetylated and also condensed with *p*-acetylaminobenzene sulphonyl chloride.

To obtain these compounds 5-nitro-N-*p* chlorophenylanthranilic acid was cyclised with phosphorus oxychloride to give 7-nitro-3:5-dichloroacridine. 7-Nitro-3:5-dichloroacridine has further been condensed with aniline, *p*-anisidine, *p*-chloroaniline, *p*-aminobenzene sulphonamide,  $\gamma$ -diethylaminopropylamine and  $\delta$ -diethylaminobutylamine according to Method I.

In the condensation of  $\epsilon$ -diethylaminoamylamine with the dichloroacridine by Method I, much of acridone was formed, consequently the condensation was accomplished according to Method II.

7-Nitro-3-chloro-5-aminoacridine was obtained by the treatment of 7-nitro-3:5-dichloroacridine with ammonium carbonate in hot phenolic solution. This 5-aminoacridine was further condensed with *p*-acetylaminobenzene sulphonyl chloride in dry pyridine.

7-Nitro-3-chloro-5(phenyl) aminoacridine and 7-nitro-3-chloro-5(4'-methoxyphenyl)-aminoacridine were further reduced by anhydrous stannous chloride, acetic anhydride and hydrochloric acid. These reduced 7-amino groups were further acetylated and also were condensed with *p*-acetaminobenzene sulphonyl chloride in dry pyridine to yield the corresponding 7-*p*'-acetaminobenzene sulphonylamino-3-chloro-5-substituted acridines.

#### EXPERIMENTAL

**7-Nitro-3 5-dichloroacridine.**—5-Nitro-*N*-*p*-chlorophenylanthranilic acid (1 g) was refluxed with excess of phosphorus oxychloride (6 c.c.) for 4 hours on an oil-bath. The oxychloride was removed by distillation under reduced pressure. The residue was triturated with cold ammonia, filtered, washed, and dried in a steam-oven. On crystallisation from dry benzene, it gave yellow needles, m. p. 208-209°. (Found N, 9.71.  $C_{13}H_8O_2N_2Cl_2$  requires N, 9.66 per cent).

**7-Nitro-3-chloroacridone**—The insoluble portion, which was left on crystallisation of 7-nitro-3 5-dichloroacridine from benzene, on washing with hot alcohol, chloroform, acetone and ether gave a product which did not melt up to 400°. This could not be crystallised from any of the organic solvents. On analysis it gave N, 10.46%, while the acridone  $C_{13}H_7O_2N_2Cl$  requires N 10.20%. So the result of analysis shows that it is 7-nitro-2-chloroacridone.

**4-Nitro-4'-chlorodiphenylamine - 6-carboxyl Chloride.**—5-Nitro-*N*-*p*-chlorophenylanthranilic acid (1 g.) was suspended in 8 c.c. of dry benzene and phosphorus pentachloride (0.9 g.) was added to it. It was refluxed for 15 minutes until a solution was obtained. On filtration and cooling, it deposited yellow powder which was crystallised from dry benzene, m. p. 135-36°, yield 80%. (Found N, 9.27.  $C_{11}H_8O_2N_2Cl_2$  requires N, 9.0 per cent).

**7-Nitro-3-chloro-5-aminoacridine**—7-Nitro-3 5-dichloroacridine (1 g) was heated with phenol (5 g) up to 70°. Then ammonium carbonate (1 g) was added slowly and temperature raised to 120° for 15 minutes. The reaction mixture was treated with ether, and dry hydrochloric acid gas passed through it. The hydrochloride after washing with acetone, was treated with sodium hydroxide solution and the base was crystallised from chloroform, m. p. 303-304°. (Found N, 15.66.  $C_{13}H_8O_2N_2Cl_2$  requires N, 15.35 per cent).

**7-Nitro-3-chloro-5-(*p*'-acetylaminobenzene sulphonyl) aminoacridine.**—The solution of 7-nitro-2-chloro-9-aminoacridine (1 g) in dry pyridine (20 c.c.) was heated to 125° for 3 hours with *p*-acetylaminobenzene sulphonyl chloride (1.4 g.). Yellow needles were deposited on cooling. It was filtered and crystallised from dry pyridine as bright yellow needles, m. p. 356-58°. (Found: N, 12.18.  $C_{21}H_{11}O_5N_2ClS$  requires N, 11.90 per cent).

**7-Nitro-3-chloro-5-substituted Acridines (Method I).**—7-Nitro-3:5-dichloroacridine (1 g., 1 mol.) was dissolved in phenol (5 g.) and the amine (1.1 mol.) to be condensed was added. The mixture was heated on a steam-bath for 3 hours. After cooling, the reaction mixture was thoroughly triturated with ether. The product was filtered

and thoroughly washed with ether. It was usually crystallised from glacial acetic acid. The free base was obtained by treatment with sodium hydroxide solution.

*7-Nitro-3-chloro-5-(phenyl) aminoacridine*.—The hydrochloride was crystallised from glacial acetic acid, m. p. 320–21°. (Found: N, 11.03.  $C_{19}H_{12}O_2N_3Cl \cdot HCl$  requires N, 10.88 per cent). The base was crystallised from 80% alcohol as orange needles, m. p. 255–56°.

*7-Nitro-3-chloro-5-(4'-methoxyphenyl) aminoacridine*.—The hydrochloride was crystallised from glacial acetic acid, m. p. 307–309° (decomp.). (Found: N, 10.30.  $C_{20}H_{14}O_3N_3Cl \cdot HCl$  requires N, 10.09 per cent). The base was crystallised from benzene, m. p. 239–40°.

*7-Nitro-3-chloro-5-(4'-chlorophenyl) aminoacridine*.—The hydrochloride was crystallised from glacial acetic acid, m. p. 332–34° (decomp.). (Found: N, 10.08.  $C_{19}H_{11}Cl_2N_3 \cdot HCl$  requires N, 9.99 per cent). The base on crystallisation from 80% alcohol yielded beautiful scarlet needles, m. p. 266–67°.

*7-Nitro-3-chloro-5-(4'-sulphonamidophenyl) aminoacridine* was crystallised from acetone, m. p. 282–83°. (Found: N, 13.23.  $C_{19}H_{13}O_4N_4ClS$  requires N, 13.07 per cent).

*7-Nitro-3-chloro-5-( $\gamma$ -diethylaminopropyl) aminoacridine*.—The condensation was effected as given in Method I, with some difference in working out the product. After trituration with ether the semi-solid obtained was treated with 2-N-sodium hydroxide solution and the free base was washed with alkali and then with water. It was separated from any acridone by treating with dilute hydrochloric acid in which the acridone was insoluble. Then the hydrochloride solution was washed with ether, the ether separated, and the remaining hydrochloride solution was filtered and again neutralised with 2N-sodium hydroxide. The free base was separated, dissolved in ether and dried over fused magnesium sulphate. The dry ethereal solution was treated with a few drops of absolute alcohol, saturated with hydrochloric acid gas. A yellow powder of dihydrochloride separated. It was thoroughly triturated with ether and crystallised from a mixture of equal quantities of alcohol and acetone as bright yellow micro-crystals, m. p. 212–14° (Found: N, 12.36.  $C_{20}H_{23}O_2N_4Cl \cdot 2HCl$  requires N, 12.10 per cent).

*7-Nitro-3-chloro-5-( $\delta$ -diethylaminobutyl) aminoacridine* was worked out as above, and crystallised from absolute alcohol as yellow glistening needles, m. p. 224–26°. (Found: N, 12.12.  $C_{21}H_{25}O_2N_4Cl \cdot 2HCl$  requires N, 11.82 per cent).

*7-Nitro-3-chloro-5-( $\epsilon$ -diethylaminoamyl) aminoacridine (Method II)*.—In this condensation by the above method, a lot of acridone was formed. 4-Nitro-4'-chlorodiphenylamine-6-carboxyl chloride (1 g.) was taken up in 10 c.c. of dry benzene, and then  $\epsilon$ -diethylaminoamylamine (0.7 g.) was added to it. The mixture was refluxed on a water-bath for 30 minutes. After this 3 c.c. of phosphorus oxychloride were added to it and refluxing continued for 6 hours. After cooling, benzene was decanted off and the residue washed thoroughly with ether. It was then taken up in 15 c.c. of hot absolute alcohol and 50 c.c. of ether were added to it. A yellow powder separated out, which was crystallised from a mixture of absolute alcohol and acetone, m. p. 235–36°. (Found: N, 11.57.  $C_{22}H_{27}O_2N_4Cl \cdot HCl$  requires N, 11.40 per cent).

*7-Amino-3-chloro-5-(phenyl)aminoacridine*.—The reducing agent was prepared by suspending anhydrous stannous chloride (7 g.) in acetic anhydride (7 c.c.) and then adding glacial acetic acid to make the volume up to 30 c.c. and then saturating with dry hydrochloric acid gas till the whole of stannous chloride went into solution.

*7-Nitro-3-chloro-5-(phenyl)aminoacridine* (1 g.) was added in small portions to 30 c.c. of the reducing agent with continuous stirring, the whole operation lasting for one hour. It was then left overnight, filtered and washed with glacial acetic acid. The free base was obtained by treating with potassium hydroxide solution. It was then washed free of alkali. After drying it was crystallised from a mixture of absolute alcohol and chloroform in bright yellow needles, m. p.  $236-37^{\circ}$ , yield 90%. (Found : N, 13.39.  $C_{19}H_{14}N_3Cl$  requires N, 13.15 per cent).

*7-Amino-3-chloro-5-(4'-methoxyphenyl)aminoacridine* was obtained by the reduction of 7-nitro-3-chloro-5-(4'-methoxyphenyl) aminoacridine by the above method and crystallised from a mixture of absolute alcohol and chloroform in yellow glistening plates, m. p.  $220-21^{\circ}$ . (Found : N, 12.44.  $C_{20}H_{16}ON_3Cl$  requires N, 12.01 per cent).

*7-Acetyl-amino-3-chloro-5-(phenyl) aminoacridine*.—7-Amino-3-chloro-5-(phenyl)-aminoacridine (0.1 g.) was heated with a mixture of acetic anhydride and glacial acetic acid (30 c.c.) on a water-bath for 15 minutes. It was then poured into ice-cold water, made alkaline with ammonia solution, filtered, washed, dried and crystallised from absolute alcohol, m. p.  $286-87^{\circ}$ . (Found : N, 11.83.  $C_{21}H_{16}ON_3Cl$  requires N, 11.61 per cent).

*7-Acetyl-amino-3-chloro-5-(4'-methoxyphenyl)aminoacridine*.—Acetylation was made as in the above case. It was crystallised from absolute alcohol as shining scarlet needles, m. p.  $258-59^{\circ}$ . (Found : N, 10.94.  $C_{22}H_{18}O_2N_3Cl$  requires N, 10.72 per cent).

*7-p'-Acetaminobenzene-sulphonylamino-3-chloro-5-(phenyl)aminoacridine*.—7-Amino-3-chloro-5-(phenyl)aminoacridine (0.2 g.) was dissolved in freshly distilled dry pyridine (8 c.c.). Then *p*-acetaminobenzene sulphonyl chloride (0.24 g.) was added to the pyridine solution and left overnight and then heated in a paraffin-bath at  $125^{\circ}$  for 2 hours. After cooling, it was triturated with 30 c.c. of water and filtered and washed thoroughly with water. It could not be crystallised from various organic solvents. For analysis it was washed thoroughly with boiling absolute alcohol, chloroform, and ether. It is an orange powder, m. p.  $262-83^{\circ}$ . (Found : N, 10.99.  $C_{27}H_{21}O_4N_4ClS$  requires N, 10.84 per cent).

*7-p'-Acetaminobenzene-sulphonylamino-3-chloro-5-(4'-methoxyphenyl) aminoacridine*.—It was prepared by the same procedure as the above compound, and crystallised as an orange powder, m. p.  $256-57^{\circ}$ . (Found : N, 10.46.  $C_{28}H_{23}O_4N_4ClS$  requires N 10.24 per cent).

The authors desire to acknowledge some preliminary work done by Mr. Gurbaksh Singh in relation to these investigations.

## VARIATION OF THE DISCHARGE CURRENT AND JOSHI EFFECT WITH TIME IN IODINE VAPOUR UNDER SILENT ELECTRIC DISCHARGE

By G. S. DESHMUKH

The time variation in the conductivity  $i$  and the associated Joshi effect  $\Delta i$  has been observed over a temperature range of 30° to 90° in iodine vapour, aged under silent discharge at 0.5 kV of 500 cycles frequency.  $i$  and  $\Delta i$  show an initial increase followed by a periodic and synchronous self-reversal. The amplitude of this reversal increases with temperature but is damped when the system is preheated for a given time period. The conductivity decreases by 10 to 25% during the rest period varied from 30 to 720 minutes. Prolonged 'ageing' enhances and stabilises  $i$ , reduced and rendered unsteady due to its discontinuation. The periodic reversal of  $i$  and its diminution immediately after the rest period is not marked during ageing of bromine vapour. This is attributed, in part, to the dependence of  $i$  and  $\Delta i$  on the behaviour of the adsorption-like boundary layer formed as a result of the interaction between the electrode (glass) walls and the excited vapour. A capacitive change occurs due to the variation in the density or/and the dielectric constant of the adsorbed phase. This, as also the characteristic 'work function' of the boundary layer and its stability with and without the applied field determines the magnitude of  $i$  and  $\Delta i$ . A progressive recovery in the conductivity of bromine vapour with the duration of the rest period is associated with the marked instability of the adsorption layer of sodium bromide as suggested by its gradual sintering at room temperature and its abrogation due to adsorption of iodine. The results are in accord with Joshi's theory of the surface origin of the 'periodic effect' and the  $\Delta i$  phenomenon and suggest that sintering of the electrode layer is an additional determinant of the conductivity and the Joshi effect.

Earlier results reported the marked influence of 'ageing' *i. e.* a time variation at a constant applied potential  $V$  in the conductivity  $i$ , on the magnitude of the Joshi effect, an instantaneous and reversible photo-variation  $\Delta i$  in excited chlorine (Deo, *Proc. Ind. Acad. Sci.*, 1945, **21A**, 76; Mallikarjunappa, this *Journal*, 1948, **25**, 197) and bromine (Deshmukh and Sirsikar, *Proc. Nat. Inst. Sci.*, 1948, **14**, 157). Extension of these observations to iodine vapour was suggested by the non-identity of the rising and falling  $V$ - $i$  characteristics observed during studies of the potential variation of  $\Delta i$  in the above system (Deshmukh, *Proc. Ind. Acad. Sci.*, 1949, **29A**, 243). The present communication reports results for the synchronous and periodic reversal of  $i$  and  $\Delta i$  in excited iodine due to 'ageing' and its marked dependence on temperature, nature of the electrode surface and the duration of 'rest period' (*vide infra*).

### EXPERIMENTAL

The general apparatus and the electrical circuit used were essentially similar as adopted previously (Deshmukh and Sirsikar, *loc. cit.*). The occurrence of ageing *i. e.* a time variation of the conductivity in dark ( $i_b$ ) of iodine vapour was studied at a series of temperatures in Siemens' type (glass) ozonisers, excited at various (fixed) applied potentials  $V$  of a given supply frequency. Iodine vapour was obtained from a glass bulb containing pure solid iodine. This was sealed serially through a capillary to the

annular space of the ozoniser. The entire system was evacuated on the topler and the ozoniser was sealed off when it maintained a satisfactory vacuum. The ozoniser and the attached bulb were enclosed in an asbestos chamber, heated electrically. The quantity of iodine in the bulb was such that even at the highest temperature employed in this series of experiments some solid phase remained. The current  $i$  was measured with a double wave, oxide rectifier type, Cambridge A. C. microammeter. The current-time curves in Fig. 1 represent only one typical set of observations obtained at 30°, 80° and 90°.

The time variation of  $i_D$  after 'preheating' the system at a given temperature was studied. The data for 'ageing' obtained without preheating are termed as normal. A representative group of results observed at 0.5 kV with and without preheating the system for 360 minutes at 80° and 90° is shown in Fig. 1.

The influence of 'rest period', *i.e.* the interval between two successive exposures to discharge, on the variation of the discharge current  $i$  after 'ageing' was also studied. Iodine vapour excited at a constant applied V was allowed to age under the discharge under normal condition and also after preheating the system at a series of temperatures for a given time period. The discharge was discontinued when the current reached a stationary stage due to ageing and was restarted at the original potential after different durations for the 'rest period' as defined above. Fig. 2 illustrates a typical set of results observed at 90° by varying the rest period from 30 to 720 minutes during the ageing of iodine vapour at 0.5 kV.

TABLE I

*'Ageing' influence on conductivity in dark and light and on the Joshi effect.*

Current indicator = Oxide rectifier type A. C. microammeter. Frequency of the A. C. supply = 500 cycles/sec. Applied potential = 0.5 kV.

Temperature = 45°.					Temperature = 80°.			
Time.	$i_D$ .	$i_L$ .	$\Delta i$ .	% $\Delta i$ .	$i_D$ .	$i_L$ .	$\Delta i$ .	% $\Delta i$ .
0 min.	40.0	39.0	1.0	2.5	50.5	47.5	3.0	5.9
10	42.0	41.0	1.0	2.3	53.5	50.5	3.0	5.6
20	46.5	45.5	1.0	2.1	62.0	58.5	3.5	5.6
30	48.5	47.5	1.0	2.0	81.0	78.0	3.0	3.7
40	51.0	50.0	1.0	1.9	86.5	84.5	2.5	2.9
50	53.0	52.0	1.0	1.8	91.0	89.5	2.5	2.7
60	57.0	56.0	1.0	1.7	88.0	85.5	2.5	2.8
70	47.0	46.0	1.0	2.1	76.0	73.5	2.5	3.2
80	38.5	37.5	1.0	2.8	65.0	63.0	2.0	3.0
90	35.0	34.0	1.0	2.9	60.0	58.0	2.0	3.3

The time variation of the associated Joshi effect, an instantaneous and reversible photo-variation  $\Delta i$  of the discharge current  $i$ , in iodine vapour was observed at a series

of temperatures under *normal* condition by allowing the system to age under the discharge at a constant exciting potential  $V$ .

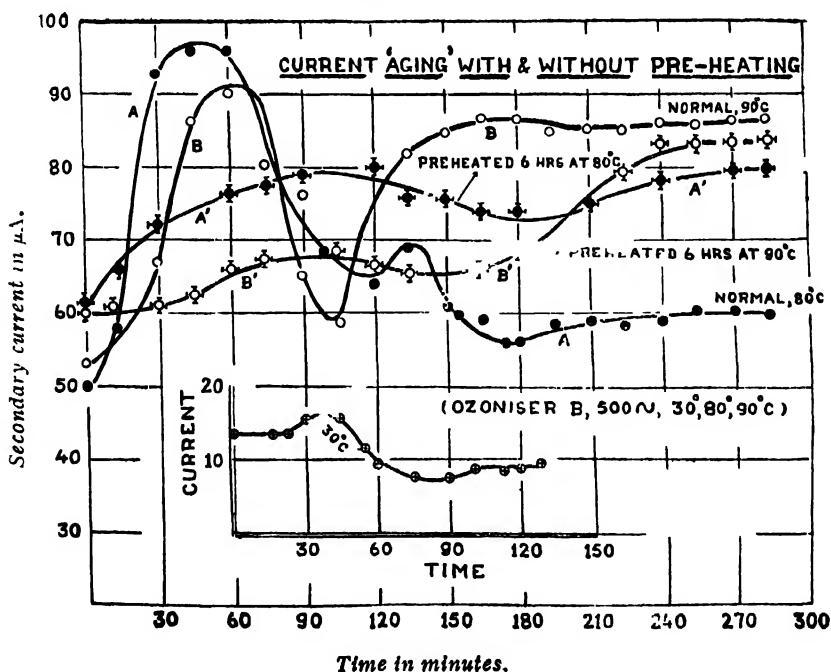
The source of irradiation consisted of two 220 volt—200 Watt incandescent (glass) bulbs. The discharge current in dark ( $i_d$ ) and that under irradiation ( $i_l$ ) were measured at different time intervals during ageing. From this the net Joshi effect ( $i_d - i_l = \Delta i$ ) and its corresponding relative value ( $100 \Delta i / i_d = \% \Delta i$ ) were calculated. Data in Table I (cf. Fig. 3) refer to only one group of results obtained by exciting iodine vapour at 0.5 kV for 90 minutes at 45° and 80°.

### DISCUSSION

The generality of the results, of which the data in Fig. 1 are but typical, suggests the following :

(a) an increase in the conductivity of iodine vapour during the initial stage ; (b) its increase ; (c) a periodic reversal of  $i$  followed by (d) the attainment of a constant stage. Thus e.g., at 80° under normal condition, the initial value of  $i$  in iodine vapour excited at 0.5 kV was 50.0  $\mu A$ . This increased due to ageing to a maximum of 92.0  $\mu A$  i. e. by about 80% in 60 minutes, and then decreased to 64.0  $\mu A$  (by 30%) in about 120 minutes. A further prolongation of ageing developed one more reversal of  $i$  of, however, a smaller amplitude till after about 210 minutes of continuous exposure to discharge,  $i$  reached a stationary stage corresponding to 56.0  $\mu A$  (cf. curve A, Fig. 1). In the other series of observations in which the system was preheated prior to the exposure to discharge for 360 minutes at 80°,  $i$  was initially 62.0  $\mu A$ . It increased to

FIG. 1



78.0  $\mu$ A (*i. e.* by about 25%) in 90 minutes and after 180 minutes of ageing it decreased to 72.0  $\mu$ A (*i. e.* by 7%). On further continuation of ageing for 240 minutes, the current increased by about 5% to a constant maximum value *viz.*, 76.0  $\mu$ A (*cf.* curve A', Fig. 1).

Results for 'ageing' at 90° with and without 'preheating' the system were on the whole similar to those mentioned above except that the amplitudes of current reversals were more pronounced and the initial and final values of *i* were larger by about 20% than those obtained at 80° (*cf.* curves B and B', Fig. 1). The time variation of *i* at 30° was much less pronounced and tended to the stationary stage after about 100 minutes of ageing under the discharge (*cf.* inset curve in Fig. 1). Compared with earlier results obtained in the case of bromine vapour (Deshmukh and Sirsikar, *loc. cit.*) excited under silent discharge under conditions similar to those maintained in the present investigation, it would appear that changes (b) and (d) are essentially common in the time variation of *i* in bromine and iodine. It is suggested that the observed decrease in htc conductivity *i* and the attainment of the stationary stage may be due to the formation and stabilisation under the discharge of an adsorption layer of iodine on the electrode (glass) walls, as postulated earlier in the case of bromine. It is, however, remarkable that the diminution in the conductivity of iodine vapour is preceded by a rapid increase of *i* during the initial stage of ageing. Furthermore, the current *i* does not reach the steady stage after its progressive diminution. The attainment of the stage (d) occurs through (c) *i. e.* a periodic reversal of *i*. The occurrence of (a) and (c) during the time variation of *i* in iodine vapour constitutes therefore a feature not observed in excited bromine. This alternating rise and fall in the conductivity, produced despite the constancy of the exciting conditions, is not consistent with the mechanism of reactions restricted to a homogeneous vapour-phase. It is therefore suggested that this periodic time variation of *i* in iodine vapour may be due to the occurrence of a complex heterogeneous reaction involving different phases with a characteristic time rate for their formation and break-up under the discharge.

At a given temperature the vapour pressure of iodine is much smaller than that of bromine. The condensibility of iodine vapour should therefore be more than that of bromine. It may be assumed that a surface layer of condensed iodine is formed primarily on the walls of the discharge tube. A partial desorption of this layer due to ionic bombardment during the initial stage of ageing, under the discharge, may lead to an increase in the concentration of the excited vapour phase and therefore to a corresponding rise in the conductivity, *i*.

The initial increase of *i* to a maximum and its diminution during ageing may also be attributed to the dissociation under the discharge of iodine vapour and its subsequent adsorption on the walls of the discharge tube. Thompson (*Proc. Roy. Soc.*, 1887, **42A**, 343) observed an appreciable and almost permanent increase of pressure during the exposure of iodine vapour to electric discharge. This he attributed to its dissociation under the discharge.

According to Joshi's equation (*Curr. Sci.*, 1947, **16**, 19) the discharge current *i* in an ozoniser circuit should increase with the increase in any one or more of the quantities,



the conduction current  $i/R_g$ , the total wall capacity  $C_w$ , and the capacity associated with the gas phase  $C_g$ . Under the operative conditions adopted in the present investigation, the mass of iodine vapour (and therefore the corresponding pressure and the threshold potential,  $V_m$ ) should increase with temperature and may not contribute to a rise in  $i/R_g$ . The gas capacity,  $C_g$  should vary synchronously with the pressure  $p$ ; an increase of  $i$  with  $p$  may therefore be anticipated.

Furthermore, it is known that the conductivity of glass is affected markedly with temperature. Manning (*Rev. Mod. Phys.*, 1940, **12**, 215) found that the conductivity of solid dielectrics increases with temperature and that a rapid rise in  $i$  suggests an incipient dielectric breakdown. This has been further illustrated by the observations of Hippel and Maurer (*Phys. Rev.*, 1941, **59**, 820) on the temperature variation of the breakdown potential of silica in the crystalline and amorphous (glass) forms. Their results show that the breakdown strength (potential) of amorphous substances like glass decreases with temperature. Presumably, the breakdown potential is identifiable or related simply to the threshold potential,  $V_m$ . At a given  $V$  the current  $i$  depends on  $V-V_m$  (Joshi, *Curr. Sci.*, 1939, **8**, 548; 1946, **15**, 281). The increase in  $i$ , observed at a constant  $V$ , may therefore be attributed to the decrease in the breakdown potential of the system with temperature.

The time variation of  $i$  may result from a corresponding change in  $C_w$ , the total wall capacity of the system, due to adsorption of iodine and the formation of adsorption complexes on the walls of the discharge tube. During exhaustive work on the dependence of adsorption on the applied potential  $V$ , Bluh (*Z. Physik*, 1931, **107**, 56, 369) found that adsorption increased if the applied  $V$  exceeded a critical value. It may be suggested that ageing of the system, under the discharge, at a constant  $V$  also facilitates the process of adsorption and that the extent of adsorption may increase with the duration of ageing. It is known that the melting point of the adsorbate is lower than that of the bulk substance. Demougin (*Compt. rend.*, 1935, **200**, 662) studied the saturation adsorption of iodine on various charcoals and on silica gel at temperatures above and below the melting point of iodine and showed that the amounts adsorbed were the same at 128°, 100° 60° and 17°. Remarkably enough, the ratio of the weights of iodine to the weight of ether adsorbed at saturation varied only from 5.0 to 5.3 for each of the seven adsorbents used. The ratio of the densities of liquid iodine and ether is 5.4, whereas that of solid iodine and liquid ether is 6.7. The adsorbed iodine simulated the liquid stage even 97 degrees below the normal melting point. Patrick and Land (*J. Phys. Chem.*, 1934, **38**, 1201) found no evidence of a melting point down to 70° i. e. even 44 degrees below the bulk melting point. This suggests that the primary adsorption layer of iodine formed during the initial stage of ageing is in the form of a surface film of semi-liquid iodine. This may react under the discharge with the glass walls of the discharge tube and lead to the formation of adsorption complexes with sodium iodide or/and iodate. Luedeking (*Chem. News*, 1890, **61**, 1) observed that the (glass) walls of the discharge tube were chiefly responsible for the absorption of iodine vapour sparked between platinum electrodes. He attributed the adsorption to the formation of sodium iodide or/and iodate.

From Maxwell's relation  $\mu^2 = K$ , data (Hodgman, "Handbook of Chemistry & Physics", Chemical Rubber Publishing Co., 28th Edition, 1944, pp. 2138, 2141, 2145) for the refractive index of glass, iodine and sodium iodide ( $\mu$  being 1.6, 3.36 and 1.77 respectively) show that the dielectric constant of iodine and sodium iodide is greater than that of glass. Since the effective wall capacity  $C_w$  increases with  $K$ , the adsorption of iodine and the formation of sodium iodide on the walls of the discharge tube should contribute to a rise in the conductivity,  $i$ .

Goetz (*Phys. Rev.*, 1929, **33**, 373) observed that the thermionic work function of the metals Cu, Ag and Au changed sharply in passing through the melting point and that the work function is larger for the phase of greater density i.e. of smaller atomic separation. Since  $\mu$  for the glass, bromine and sodium bromide is about 1.6, the dielectric constant  $K$  and the corresponding wall capacity  $C_w$  should not change appreciably due to the adsorption of bromine and the formation of sodium bromide due to ageing. The density of sodium bromide is, however, greater than that of condensed bromine (Hodgman, *loc. cit.*, pp. 357, 456). A surface film of NaBr, formed during ageing under the discharge, would increase the work function at the boundary layer. The decrease in the conductivity  $i$ , observed in excited bromine (Deshmukh and Sirsikar, *loc. cit.*), should therefore follow. On the other hand, the density of liquid iodine and NaI is less than that of solid iodine (Hodgman, *loc. cit.*, pp. 392, 460); the formation of an adsorption layer of semi-liquid iodine or/and NaI under the discharge may reduce the work function at the electrode surface and lead to the observed increase in  $i$ . The conductivity may increase to a maximum till the electrode surface (s) is covered completely with the primary adsorption layer of iodine or/and NaI. Further adsorption of iodine on the surface of the primary layer, during prolonged ageing of the system under the discharge, may decrease the work function and reduce  $i$  as observed. Baedekar (*Ann. Physik*, 1907, **22**, 756; 1909, **29**, 566) reported a marked increase in the conductivity of cuprous iodide mixed with an excess of iodine. This was not due to the internal adsorption of the electropositive atoms able to emit their valence electrons but to the taking up of an electronegative element. Tubandt (*Z. anorg. Chem.*, 1920, **110**, 234) extended these observations to other cuprous halides and showed that their conductivity also increased by the adsorption of an excess of halogen. Other electronegative elements like sulphur and oxygen, when added to certain sulphides and oxides, enhanced the conductivity appreciably; the influence on the conductivity of cuprous oxide by the taking up of oxygen has been especially studied thoroughly by many investigators. According to Wagner (*Phys. Z.*, 1931, **32**, 641) the excess electronegative element in the lattice forms excess negative ions so that just as many of the positive ions must carry a higher charge. Thus in the case of cuprous iodide, extra  $I^-$  ions are formed in the lattice and an equally large number of  $Cu^{++}$  ions. These are responsible for the electronic conduction. They are one electron short and capture an electron from a  $Cu^+$  ion which in turn is transformed into a  $Cu^{++}$  ion characteristic of the 'defect conduction'. It is interesting to note, however, that with an increased concentration of electronegative element, the conductivity decreases at high temperatures. This has been observed in the case of  $CuI$ ,  $Cu_2O$  and also in some semi-conductors like  $Ag_2O$  which are provided with an extra amount of electropositive element (Boer, *Chem. Weekblad*, 1935, **32**, 106).

Joshi (*Curr. Sci.*, 1946, **15**, 281) has emphasised the significance of the data for the time variation of  $i$  as a means of elucidating the course of a discharge reaction, especially when the determination of the change of gas pressure and a time to time analysis of the products of reaction are not feasible. He has attributed the time variation in the conductivity  $i$  to a change in the intensity of the field at the electrode surface or/and to the formation of the products of reaction of 'limited life'. According to him the surface activity of some of the reaction products may lead to the formation of an adsorption-like electrode layer. A capacitive change resulting from the formation of this layer would affect the conductivity  $i$  of the system. The periodic variation of  $i$  may be associated with an intermittent sorption and desorption of the above layer or/and the formation and decomposition under the discharge of unstable intermediate products of reaction at the surface. The production, at a constant applied  $V$  and temperature, of a spontaneous and long sustained 'periodic effect' during the decomposition of nitrogen dioxide (Joshi, *Proc. Indian Sci. Cong.*, 1943, Part II, pp. 70-75) and in the  $N_2O-H_2$  (Joshi and Deshmukh, *Nature*, 1945, **155**, 483) and  $S-N_2$  (Deshmukh and Sirsikar, unpublished data) reactions under silent discharge are explicable with the above mechanism. On this view the reversal of  $i$  during the later part of 'ageing', indicative of a like variation in  $C_u$  and  $C_{u_1}$ , may be attributed to the partial desorption of the adsorbed layer of iodine or/and the surface decomposition of unstable adsorption complexes with  $NaI$  or/and  $NaIO_3$ . It may be emphasised that a sensibly large rise in the conductivity has been observed in these laboratories during the decomposition, under the discharge, of an annular film of  $KI$ , in vacuum.

The attainment of the stationary stage in the conductivity may be envisaged as the stabilisation of the adsorption layer under the influence of the applied fields. It is very likely that the dissociation of iodine vapour and the conductivity of glass are enhanced as a result of preheating the system at high temperatures. This preheating is not favourable to the formation of a stable adsorption layer. The value of  $i$  is therefore large, but the amplitudes of current fluctuations are comparatively much less pronounced than those observed under normal conditions.

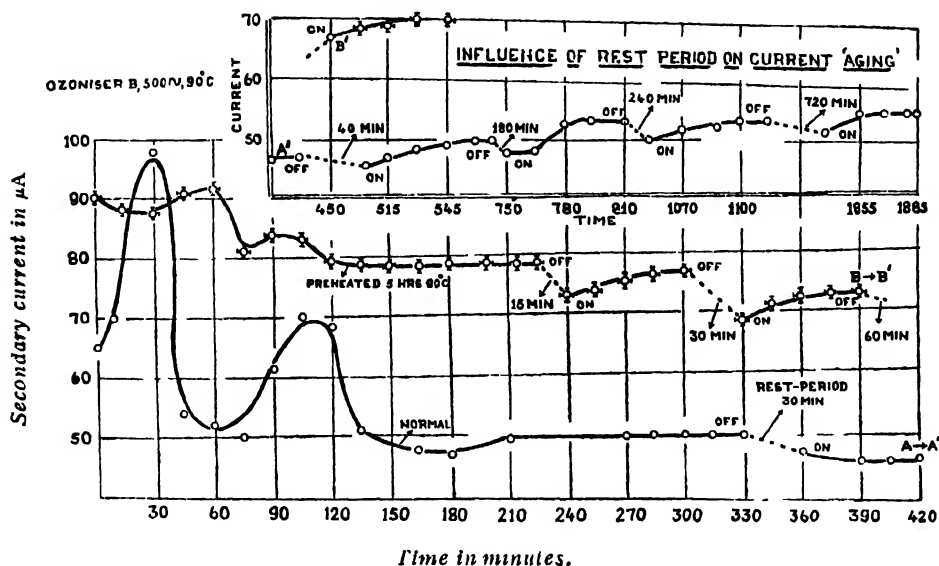
The thermal effects, mentioned above, leading to the increase of  $i$  in a solid phase are low at ordinary temperature. For this reason, and also since the vapour pressure of iodine is but small (0.47 mm.) at  $30^\circ$ , the smaller value of  $i$ , as observed, follows. The comparatively even character of the corresponding current-time curve (cf. inset curve in Fig. 1) may therefore be associated with the greater stability of the adsorption layer due to moderately low temperature.

Fig. 2 shows the influence of 'rest period' of different durations on the variation of  $i$  in iodine vapour, aged under the discharge at 0.5 kV with and without preheating the system at  $90^\circ$ .

It is seen that under normal conditions  $i$  reaches the stationary stage of  $50.0\mu A$  in about 210 minutes and remains sensibly steady on further prolongation of ageing for 330 minutes. The discharge was discontinued at this stage and was restarted after a rest period of 30 minutes. It is interesting to note that after the rest period the

current was unsteady and reached the stationary stage on the continuation of ageing for about 60 minutes. A series of successive rest periods of 40, 180, 240 and 720

FIG. 2



minutes' duration were employed after  $i$  was stabilised previously due to ageing. It is significant to observe that as a result of discontinuation of the discharge during the rest period the discharge current decreases by about 10 to 20% and tends to a steady stage only after prolonged ageing. The results obtained after preheating the system at  $90^\circ$  for 300 minutes and employing different durations of rest period are similar to those mentioned above; the amplitude of current variation is, however, less pronounced and  $i$  is larger by about 40% than that observed under normal condition (cf. Fig. 2).

It is suggested that the stabilisation of the adsorption layer due to the adsorption-desorption equilibrium, produced under prolonged ageing of the system under the discharge, leads to the stage of steady conductance. In the absence of the electrical field (i.e. during the rest period) this equilibrium is shifted so as to favour adsorption; this may reduce the conductivity  $i$  as observed. A partial desorption of the adsorption layer due to the ionic bombardment after the rest period should reduce the work function at the boundary layer and increase  $p$ ,  $C_w$  and  $C_o$ . A corresponding rise in  $i$  should therefore follow.

Earlier results in the case of bromine vapour (Deshmukh and Sirsikar, *loc. cit.*) showed that  $i$  increased partially or fully to its initial value after a given rest period. This was ascribed, in part, to the desorption of the adsorbed vapour. It is instructive to consider the influence of external factors, especially temperature, on the behaviour of surface films. The nature of the surface of the adsorbant is altered by heating. The process of increasing the surface is called activation, that of decreasing it by heat

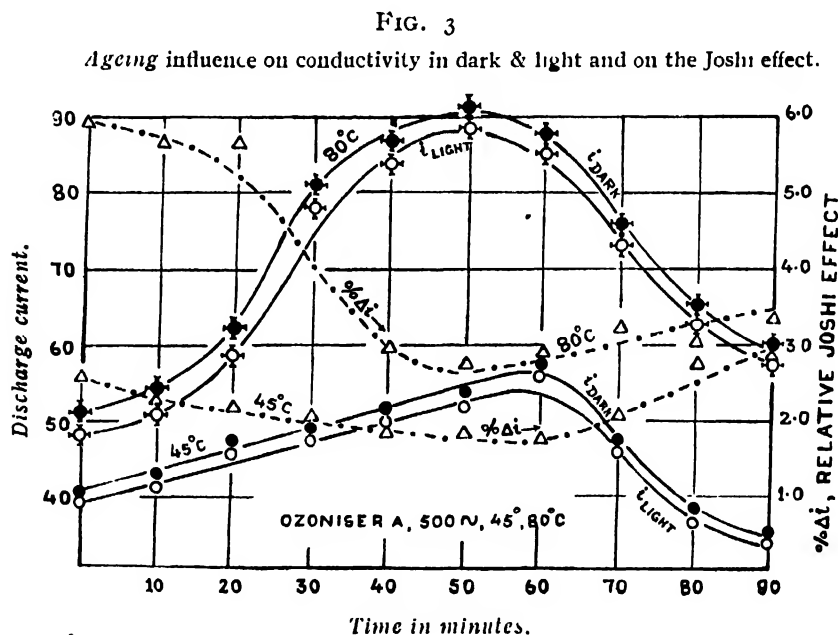
is termed as 'sintering'. 'Every adsorbent sinters if heated to high enough temperatures' (Brunauer, "Physical Adsorption of Gases and Vapours", Oxford, 1943, p. 357). This is attributed to the growth of the particle size due either to changes in the physical or chemical nature of the surface. Boer and Dippel, (*Z. physikal. Chem.*, 1933, **B21**, 198) observed the marked suitability of thin transparent films of inorganic salts, obtained by sublimation in a high vacuum, for the study of the absorption of light by matter in the adsorbed state. The adsorption of iodine on one of these salt films (e. g. calcium fluoride) gives only a monomolecular covering. The fact that the colour of adsorbed iodine can still be seen is due to the laminary structure of the salt film whereby many monomolecular layers of adsorbed iodine lie one behind the other in the path of light (Boer, *Z. physikal. Chem.*, 1932, **B15**, 300). By heating at temperatures between  $150^{\circ}$  and  $350^{\circ}$  a decrease in the surface of the salt film takes place due to sintering. During the process the film remains clear; the laminae merely become firmly attached to each other so that the interlaminary surface is considerably decreased and a number of active spots disappears. In the adsorption of iodine the amount adsorbed is very much decreased and the number of active spots that have disappeared is large compared to the decrease in the total surface. The forces which hold the surfaces of the laminae together after sintering are considerably weaker than those which act within the salt lattice. Molecules and atoms which are especially strongly adsorbed abrogate the effect of sintering. Thus the film of calcium fluoride sintered at temperatures not higher than  $350^{\circ}$  is completely broken up by the adsorption of caesium and the original value of the adsorption of iodine can be measured (Boer and Dippel, *Chem. Weekblad*, 1933, **30**, 78, 221).

Compared with the films of calcium or barium halides, the layers of alkali halides are more easily sintered. A film of sodium bromide sinters gradually even at ordinary room temperature. In this case the opening of the film is also easier; the adsorption of iodine leads to the opening of the sintered film of NaBr (Boer, "Electron Emission and Adsorption Phenomena", Cambridge, 1935, p. 188). The initial decrease in the conductivity  $i$  of excited bromine has been attributed to the adsorption of bromine vapour on the walls of the discharge tube. It is likely that a surface film of sodium bromide is formed under the discharge due to the interaction of the adsorbed vapour and the electrode (glass) walls. A gradual sintering of this layer during the rest period may lead to a rise in the concentration of the active vapour phase and therefore to a corresponding increase in the % restoration of  $i$  with the duration of the rest period. The decrease of  $i$ , as observed in the present investigation, after each successive rest period, suggests that unlike bromine or/and NaBr the adsorption layer of iodine and NaI, formed during ageing of iodine vapour under the discharge, is comparatively stable. The relative stability of NaBr and NaI, as judged by the data for their thermal decomposition, however, shows that the former is more stable than the latter. That, this perhaps may not be the only criterion for determining the stability of the compounds, especially in the adsorbed state, is suggested by the observation that the adsorbed film of NaBr sinters even at the ordinary room temperature. Furthermore, the abrogation of the sintered layer of NaBr by the adsorption of iodine

supports the assumption that the surface film of NaI may be more stable than that of NaBr.

In the absence of the exciting field the adsorption layer of iodine or/and NaI may catalyse the recombination of the iodine atoms and lead to an increase in the threshold potential,  $V_m$  or/and decrease  $C_w$ , the effective capacity of the annular walls. This may reduce the conductivity  $i$  due to the rest period.

According to Joshi's theory (*Proc. Indian Sci. Cong.*, 1946, Part III, *Phys. Sec.*, Abst. No. 26) an adsorption like boundary layer, formed from the wall adsorption of the ions and molecules of the excited gas, is the chief seat of  $\Delta i$ . Photoelectrons emitted from this layer due to external irradiation are captured by the excited gas particles to give slow moving negative ions and produce the photodiminution  $\Delta i$  as a space charge effect. Since the probability of electron capture by a particle depends on  $P/E$ , where  $P$  is the pressure and  $E$ , the electrical field, the favourable effect of  $P$  at constant  $E$  on the magnitude of  $\Delta i$  follows. Results in Table I (cf. Fig. 3) show that the discharge current in the dark ( $i_d$ ) increases initially, reaches a maximum and then decreases as a result of ageing the system under the discharge at 0.5 kV. The curve for  $i_d$  in Fig. 3 does not, however, represent the time variation of  $i$  under light. The points



on the line denote the values obtained for  $i$  when the system is irradiated for 30 seconds at different intervals during ageing. The net Joshi effect  $\Delta i$  is sensibly constant at low temperatures but varies periodically and synchronously with  $i$  at comparatively high temperatures. Thus e. g., at 80° and 0.5 kV,  $i$  increased by 15% in 15 minutes of exposure to discharge and decreased by about 45% on further continuation of ageing for 90 minutes (cf. Table I). The relative effect, % $\Delta i$ , decreased initially to a minimum and increased again when  $i$  and  $\Delta i$  were decreasing. The initial increase

of  $i$  has been attributed, in part, to the desorption of iodine vapour adsorbed primarily on the walls of the discharge tube. Since  $p$ , and therefore  $C_a$ , increases during desorption, a corresponding rise in  $i$  and  $\Delta i$  should ensue. The variation in  $p$  is less pronounced at low temperatures due to the greater stability of the adsorption layer. The net Joshi effect  $\Delta i$  is therefore sensibly constant at  $45^\circ$  (cf. Table I and Fig. 3). The above suggestion can only be a partial explanation since the variation in  $i$  and  $\Delta i$  is far larger than the corresponding changes in  $p$  and  $C_a$  due to desorption. Previous results in the case of chlorine (Joshi and Deo, *Nature*, 1944, **154**, 343) showed that, within limits, the relative Joshi effect  $\% \Delta i$  increases from a low value to almost 93% current diminution under light with  $p$ . It is also remarkable that a practically 100% Joshi effect occurs in Hg vapours excited under topler vacuum (0.001138 mm. Hg). Similarly the Joshi effect, as large as 60% to 70%, has been observed in sulphur and selenium vapour (vapour pressure being 0.0003 and 0.0008 mm. at  $49^\circ$  and  $193^\circ$  respectively). This suggests that compared with changes in  $p$ , the nature and behaviour of the adsorption-like boundary layer is a more important determinant of the magnitude of  $\Delta i$ . The formation of the primary adsorption layer of iodine or/and NaI and the resultant change in the density of the adsorbed phase may reduce the work function at the boundary layer. The total wall capacity,  $C_w$ , and therefore  $i$  and  $\Delta i$  should increase as a consequence. The increased adsorption of iodine and the growth of secondary adsorption layers due to the prolonged ageing should reduce  $p$ ,  $C_a$ ,  $C_w$  and increase the work function at the electrode surface. This may lead to a corresponding reduction in  $i$  and  $\Delta i$  as observed. Studies of the potential reversibility of the Joshi effect,  $\Delta i$ , in iodine vapour (Deshmukh, *loc cit.*) have shown that its magnitude and even sign is affected by but a small change in the applied V, and that the production of the positive Joshi effect  $+\Delta i$  is favoured by high temperature and low applied potential. In the present series of experiments, the negative Joshi effect  $-\Delta i$  has been observed in iodine vapour excited at 0.5 kV at  $90^\circ$ . It may be assumed that excitation of the system at the above potential facilitates the formation of slow moving negative ions and masks the positive effect  $+\Delta i$ .

In conclusion, the author wishes to express his grateful thanks to Prof. S. S. Joshi for his keen interest and valuable guidance during the work.

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## STUDIES OF JOSHI EFFECT IN HYDROGEN

BY K. S. VISVANATHAN

Production of the Joshi effect in  $H_2$  under ozoniser excitation has been studied in respect of (i) gas pressure (20-200 mm.), (ii) temperature ( $15^\circ$ - $55^\circ$ ), (iii) frequency and intensity of incident light, (iv) applied potential (0.67-2.13 kV), (v) frequency of A. C. supply, and (vi) ageing. Under favourable conditions, the system shows Joshi effect of as much as 50% current diminution under but visible light. As generalised by Joshi, the relative Joshi effect,  $-\% \Delta i$ , is (numerically) maximum at  $V_m$ , the threshold potential and decreases thereafter. Gas pressure shows a limiting influence. Increase of (ii) and (v) decreases, while that of (iii) increases the effect. Moderate 'ageing' under the discharge due to a high potential, followed by allowing the system to stand over for limited periods, enhances the effect. Evidence has been adduced to show that the Joshi effect is not a consequence of selective absorption, nor due to destruction of metastable atoms under irradiation. These findings are in accord with Joshi's general theory of the phenomenon.

The discovery of the Joshi effect is the outcome of a programme of research initiated in the chemical laboratories of the Benares Hindu University on the study of the behaviour of gases, elemental and compound, when subjected to silent and other type of electrical discharge (Joshi, *Curr. Sci.*, 1939, 8, 548; Joshi and Narasimhan, *ibid.*, 1940, 9, 536; Joshi, *Proc. Indian Sci. Cong.*, 1943, Part II, pp. 70-75). The general finding of Joshi's that (i) a gas is characterised by a minimum threshold potential,  $V_m$  at/near which it breaks down as a dielectric and shows a sudden increase in conductivity (Joshi, *Nature*, 1944, 154, 147), (ii) that in a compound gas, a reaction is induced only when the applied potential equals or exceeds  $V_m$  (*loc. cit.*), and (iii) that irradiation of the reaction vessel, which is an all-glass Siemens' ozoniser or a semi-ozoniser of wire-in-cylinder type, results in a rise in  $V_m$  of the system, led Joshi to the anticipation and discovery of the Joshi effect, viz., that  $i$ , the discharge current at a definite applied potential, shows an instantaneous and reversible variation (usually a decrease),  $\Delta i$  on irradiation (Joshi, *Proc. Ind. Acad. Sci.*, 1945, 22A, 389). Most of the early work was confined to  $Cl_2$  in which the effect was first observed and in which it was considerable, being as much as 93-95% of  $i$  under optimum conditions (Joshi and Deo, *Nature*, 1944, 153, 434). Subsequent investigation of other systems has led to the belief that the effect is considerable in the other halogens also, and is in the order:  $Cl_2 > Br_2 > I_2$  and that it is practically negligible in other gases such as  $H_2$ ,  $N_2$ , air, etc. (Joshi and Deshmukh, *Nature*, 1941, 147, 806) and metallic vapours such as Hg.

Recent work with improved technique as regards current detection and measurement, which has resulted in the use of sensitive galvanometers actuated by metal oxide rectifiers or thermionic valves of different types, and the careful examination of the influence of a number of factors, which control and determine the magnitude of the Joshi effect, (*vide infra*) have revealed the occurrence of the effect to a marked extent in almost all gases, both elemental and compound, and metallic vapours, e.g.,  $O_2$ ,  $HCl$ ,  $NO_2$ , air,  $SO_2$ ,  $H_2$ , water vapour,  $NH_3$ , Hg, Na, K, S, Se, As, etc. From a study of the nature and magni-



tude of the Joshi effect in the halogens and other gases, and its dependence on a number of electrical factors and the nature of irradiation etc., Joshi has advanced a theory for the phenomenon (*Proc. Indian Sci. Cong.*, 1946, *Phys. Sec.*, Abst. No. 25 ; *Curr. Sci.*, 1947, **16**, 19). The theory contemplates a close connection between the Joshi effect and the 'electron affinity' of the gas, which is one of its chief determinants. Whilst then the occurrence of a pronounced Joshi effect in the halogens, which possess a large electron affinity (3.22 to 3.70 e.v.), is easily understood, contrary to the preliminary results, an appreciable Joshi effect also in  $H_2$  is to be anticipated since its electron affinity, 0.76 e.v., is not inconsiderable (Massey, "Negative Ions", The Cambridge Physical Tracts, 1938 ; Glocker, *Phys. Rev.*, 1934, **45**, 111).

Preliminary work by the author (Visvanathan and Raghavan, *Proc. Ind. Acad. Sci.*, 1947, **29A**, 98) on  $H_2$  under silent electric discharge at 500 cycles frequency has indicated that the gas shows no Joshi effect at pressures less than 252 mm., while at 252 mm. it gives a positive effect of 400% just below  $V_m$ . While the fresh gas at 50 mm. shows no Joshi effect, 'ageing' at an applied potential of 0.40 kV for different periods produces first the negative effect of small magnitude, about 5% decrease of the discharge current in the dark, as the time of ageing increases, the system develops larger and larger positive effect which ultimately reaches the high value of about 8 times the photoincrease of the discharge current. Admixture of  $H_2$  with  $Br_2$  which taken alone gives a marked negative Joshi effect, which is to be anticipated from its large electron affinity, modifies the behaviour of  $Br_2$  so that the greater the amount of  $H_2$  in the mixture, the larger is the positive effect observed.

In view of the above interesting behaviour of 'aged' and of admixed  $H_2$  with regard to the production of the Joshi effect, it was thought desirable to study comprehensively the production of the phenomenon in pure  $H_2$  with a careful appraisal of the influence of the various factors which affect it viz., (i) applied potential and gas pressure, (ii) ageing of the system and frequency of the A. C. supply, (iii) intensity and (iv) frequency of the incident light, and (v) temperature, for which there is no information in the literature on the subject except the preliminary communication by the author. Since increase of frequency of the A. C. supply is found to reduce the magnitude of the Joshi effect (Joshi, *Curr. Sci.*, 1945, **14**, 67), alternating current of 50 cycles per second has been employed in the present investigation as against 500 cycles used earlier.

## EXPERIMENTAL

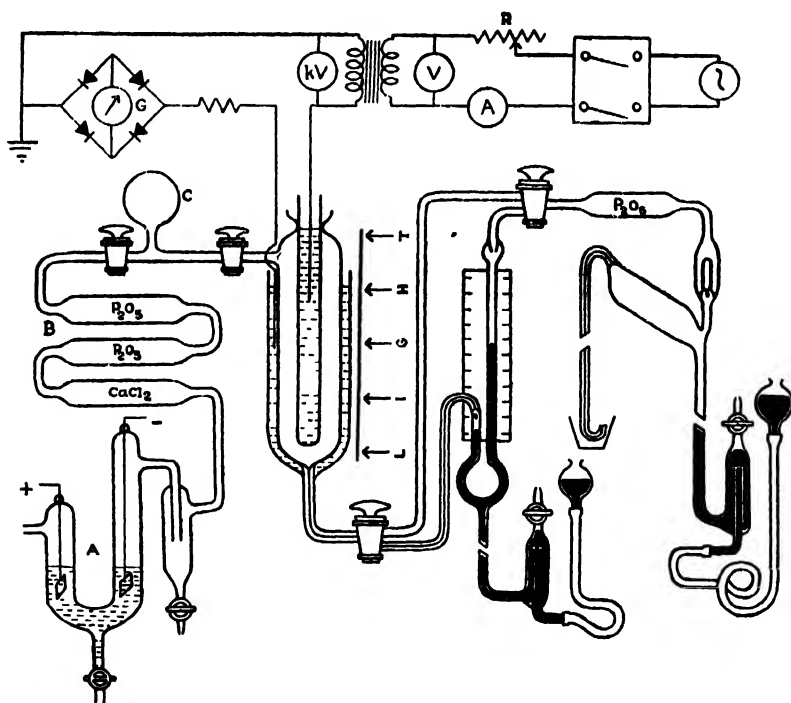
The apparatus (Fig. 1) consists essentially of three parts, viz., (i) arrangement for the electrolytic preparation, drying and storage of  $H_2$ ; (ii) discharge tube and electrical connections, and (iii) arrangement for the irradiation of the ozoniser. Since the apparatus is essentially the same as described in some of the previous publications on the Joshi effect, its full description is not given here. Only important points in which the present set-up of the apparatus differs from the others are mentioned.

**Preparation and Storage of the Gas.**—A saturated solution of barium peroxide (Merck, ex. pure) was prepared with  $CO_2$ -free water and electrolysed in a U tube A

one limb of which containing the negative electrode at which  $H_2$  was evolved, being about twice as long as the other. The electrodes were of platinum foils and the current was adjusted so as to give a slow evolution of  $H_2$  and  $O_2$ . The gas was led through drying tubes *B* containing fused  $CaCl_2$  and  $P_2O_5$  and stored in the gas holder, *C*.

*Discharge Tube and Electrical Connections.*—An all-glass Siemens' ozoniser was used as the discharge vessel. Single phase alternating potentials of frequency of 50 cycles per second, obtained from a rotary converter worked off the 220-volt D. C. mains, were stepped up by means of a transformer and maintained at the desired value by regulation of the external resistance, *R*, of the primary circuit. One terminal of the transformer was earthed, while the other, the high tension terminal, was connected to the inner electrode of the ozoniser. The circuit was completed by connecting the outer electrode to earth through the current-measuring device, viz., a metal oxide rectifier and a sensitive mirror galvanometer provided with a shunt of non-inductive resistance made of straight silver wire. The deflexions of the galvanometer, as a measure of the discharge current, were read from a scale bent in the form of an arc of radius of about one meter from the galvanometer.

FIG. 1



*Irradiation of the Ozoniser.*—The ozoniser was irradiated by a system of two 200-Watt and one 80-Watt bulbs which were connected in series with a resistance by the adjustment of which a constant potential of 180 volts was applied to the bulbs in order

to maintain the intensity of illumination constant. The bulbs were enclosed in a wooden box, the side facing the ozoniser being of the nature of a shutter ; the ozoniser could thus be irradiated or kept in dark as desired.

*Influence of Applied Potential and Gas Pressure*

H<sub>2</sub> was introduced into the ozoniser at a pressure of 200 mm. and exposed to a very low applied potential which was raised gradually to higher values. The current in the earlier stages, as measured by the milliammeter and the deflexion of the galvanometer, was very small, almost negligible. When the applied potential reached a critical value viz., the threshold potential,  $V_m$ , there was a sudden, large increase in the current and the gas began to glow faintly. Irradiation of the ozoniser containing the gas produced no change in the current at potentials less than  $V_m$ , while at  $V_m$ ,  $i_0$ , the discharge current in the dark, showed an instantaneous and reversible decrease to  $i_L$ , the current under irradiation. The above observations are in line with those reported from these laboratories (Joshi, *Nature*, 1944, **154**, 147 ; *Can. Sci.*, 1944, **13**, 253, 278 ; *Proc. Ind. Acad. Sci.*, 1945, **22A**, 225). The net Joshi effect,  $\Delta i$  ( $= i_L - i_0$ ) and the relative Joshi effect,  $\% \Delta i$  ( $= 100 \Delta i / i_0$ ) have been calculated. In general, the discharge current ranged between 0.01 and 0.3 milliamp. for the range of applied potentials studied. Since it was not possible to measure accurately the current changes, especially at low potentials, owing to limitations of the available milliammeter,  $i_0$ ,  $i_L$  and hence  $\Delta i$  were measured in terms of the deflexions of the galvanometer, from which the relative Joshi effect,  $\% \Delta i$ , has been calculated. In the present investigation, H<sub>2</sub> gave only the negative effect,  $-\Delta i$  and  $-\% \Delta i$  and for purposes of comparison their numerical values alone have been employed.

The variation of the Joshi effect with the pressure of the gas was studied by abstracting from the ozoniser hydrogen till the pressure was reduced to the next required value viz., 150 mm. at which pressure the potential variation of the Joshi effect was again studied. Thus, the different pressures at which such studies were made were obtained by pumping out part of the gas in stages till a pressure of 15 mm. was reached. The pressures thus studied are 200, 150, 124, 108, 90, 80, 70, 60, 50, 40, 30 and 20 mm. The results are given in Table I.

TABLE I

*Potential variation of relative Joshi effect,  $\% \Delta i$ , in hydrogen.*

(a) $p_{H_2} = 200$ mm.		(b) $p_{H_2} = 150$ mm.		(c) $p_{H_2} = 124$ mm.		(d) $p_{H_2} = 108$ mm.	
kV.	$-\% \Delta i$ .	kV.	$-\% \Delta i$ .	kV.	$-\% \Delta i$ .	kV.	$-\% \Delta i$ .
1.34	9.5	1.07	15.8	1.07	20.5	0.67	22.8
1.60	1.7	1.34	6.1	1.34	7.8	1.07	22.1
1.87	0.5	1.60	1.7	1.60	2.4	1.34	13.4
		1.87	0.5	1.87	1.4	1.60	6.0
						1.87	3.4

TABLE I (contd.)

(e) $p_{H_2} = 90$ mm		(f) $p_{H_2} = 80$ mm		(g) $p_{H_2} = 70$ mm		(h) $p_{H_2} = 60$ mm.	
kV.	$-\% \Delta i$ .	kV	$-\% \Delta i$	kV	$-\% \Delta i$ .	kV.	$-\% \Delta i$ .
0.67	19.8	0.67	20.6	0.67	23.8	0.54	38.7
1.07	14.5	1.07	12.6	1.07	12.3	0.67	28.9
1.34	8.9	1.34	8.3	1.34	6.9	1.07	14.6
1.60	6.3	1.60	4.5	1.60	4.2	1.34	6.8
1.74	5.2					1.60	4.6
(i) $p_{H_2} = 50$ mm,		(j) $p_{H_2} = 40$ mm.		(k) $p_{H_2} = 30$ mm		(l) $p_{H_2} = 20$ mm,	
kV	$-\% \Delta i$ .	kV.	$-\% \Delta i$	kV.	$-\% \Delta i$	kV	$-\% \Delta i$ .
0.54	31.6	0.54	50.0	0.54	48.4	0.51	24.2
0.67	26.3	0.67	34.5	0.67	31.8	0.67	1.7
1.07	12.8	1.07	16.9	1.07	9.9	1.07	0
1.31	7.1	1.31	7.2	1.34	5.1	1.34	0
1.60	3.7	1.60	3.0	1.60	2.6		

It is seen from Table I that for any particular pressure of the gas, the relative effect,  $\% \Delta i$ , is (numerically) maximum at the lowest potential indicated viz., the threshold potential,  $V_m$  and decreases as the potential increases. This characteristic behaviour of the relative Joshi effect has been observed in numerous other systems as well (Joshi, *Proc. Ind. Acad. Sci.*, 1945, **22A**, 389).

The variation of  $\% \Delta i$  with the pressure of the gas may be illustrated by the following readings.

Pressure (mm) :	200	150	124	108	90	80	70	60	50	40	30	20
At 1.34 kV, $\% \Delta i$	9.5	6.8	7.8	13.4	8.9	8.3	6.9	6.8	7.4	7.2	5.1	0
At 1.60 kV, $\% \Delta i$ :	1.7	1.7	2.4	6.0	6.3	4.5	4.2	4.6	3.7	3.0	2.6	0

While maximum effect is obtained at 108 mm. of the gas at both the applied potentials, the influence of the latter is brought out by the fact that  $\% \Delta i$  is less at 1.60 kV than at 1.34 kV at all pressures. Below a pressure of 30 mm. the gas shows no Joshi effect.

Instead of comparing the values of  $\% \Delta i$  at any arbitrary applied potential, they, in accordance with the concept of 'corresponding potentials' developed by the author in his paper on Joshi effect in air (unpublished), are compared at the threshold potential,  $V_m$  of the various pressures; the results stand out more significantly. Thus,

Pressure of $H_2$ :	200	150	124	108	90	80	70	60	50	40	30	20
$-\% \Delta i$ at $V_m$ :	9.5	15.8	20.5	22.8	19.8	20.6	23.8	38.7	31.6	50.0	48.4	24.2

The limiting effect of pressure on  $\% \Delta i$  is clear from the above figures.

It may be recalled that in the above series of experiments,  $H_2$  was taken at the maximum pressure of 200 mm. and the subsequent pressures were obtained by pumping out part of the gas. As the lower pressures were being reached, a certain amount of ageing of the gas under discharge might have occurred and the behaviour of this aged gas might be different from that of a fresh sample of the gas. To investigate this possibility, the potential variation of the Joshi effect at different pressures was determined again, using a different procedure in the following experiments.

$H_2$  was taken at a low pressure viz., 30 mm. and the potential variation of the Joshi effect carried out. Fresh gas was now admitted till the pressure rose to the next required value, viz., 45 mm. In this way the potential variation of  $\% \Delta i$  was studied at each pressure which was increased in the above manner by admitting additional fresh gas from a given stock of the purified gas. The results are indicated in Table II.

TABLE II

*Potential variation of relative Joshi effect,  $-\% \Delta i$ , in hydrogen.*

(a) $p_{H_2} = 30$ mm		(b) $p_{H_2} = 45$ mm		(c) $p_{H_2} = 60$ mm	
kV.	$-\% \Delta i$	kV	$-\% \Delta i$	kV	$-\% \Delta i$
1.01	1.2	0.80	0.8	0.91	21.4
1.23	0.9	0.91	1.6	1.07	41.9
1.33	0.8	1.07	1.8	1.23	20.9
1.49	0.6	1.23	1.3		
		1.33	0.9		
		1.49	0.7		
		1.76	0.7		
(d) $p_{H_2} = 70$ mm		(e) $p_{H_2} = 90$ mm		(f) $p_{H_2} = 100$ mm	
kV	$-\% \Delta i$	kV	$-\% \Delta i$	kV.	$-\% \Delta i$
0.91	36.5	0.91	20.0	0.8	4.1
1.07	41.1	1.07	42.3	1.07	20.1
1.23	43.6	1.33	25.7	1.17	16.6
		1.49	20.0	1.28	13.3
				1.39	9.2
				1.49	7.9
				1.60	7.3
(g) $p_{H_2} = 120$ mm		(h) $p_{H_2} = 150$ mm.		(i) $p_{H_2} = 200$ mm.	
kV.	$-\% \Delta i$	kV	$-\% \Delta i$	kV.	$-\% \Delta i$
0.75	17.2	1.07	4.9	1.44	0.6
0.80	28.6	1.17	5.7	1.60	0.7
1.07	39.0	1.28	7.1	1.71	0.8
1.34	13.0	1.39	3.2		
		1.49	0.6		
		1.60	0.7		

It is striking, in general, to note the very low values of  $\% \Delta i$  in this series of experiments. It was observed that  $V_m$  of the system was not as sharp as in the previous series of experiments, and what is more, for a particular pressure,  $\% \Delta i$  unlike in the previous series of experiments shows its maximum value not at/near  $V_m$  but at some intermediate potential above which it decreases. It should be remembered that in this series of experiments the gas is actually a *mixture* of aged gas, *i.e.*, gas already subjected to exciting potentials for various periods, and fresh gas, while in the previous case it was *pure* (though aged) in that it was of one sample taken. It would then appear that while a 'pure' gas has a sharp  $V_m$  at which the negative Joshi effect is maximum, a mixture of gases is not characterised by a sharp  $V_m$  and  $\% \Delta i$  starts from low values to reach a maximum and then declines, as the applied potential is continuously increased. The above deduction is borne out by results obtained for the Joshi effect in a mixture of  $\text{Br}_2$  and  $\text{Cl}_2$  by Visvanathan and Raghavan (*loc. cit.*). Below are given the maximum values of  $\% \Delta i$  observed at each pressure with the corresponding applied potential.

Pressure (mm) :	30	45	60	70	90	100	120	150	200	225
kV :	1.01	1.07	1.07	1.23?	1.07	1.07	1.07	1.28	1.71	...
Max. $\% \Delta i$	1.2	1.8	44.9	43.6	42.3	22.1	39.0	7.1	0.8	0

It is seen in the above case that though the values of kV quoted do not represent  $V_m$  of the system, the limiting effect of the pressure on the magnitude of the Joshi effect persists. The abrupt rise in the effect from 1.8% at 45 mm. to 44.9% at 60 mm. is striking and is under further detailed investigation.

#### *Influence of Ageing on the Joshi Effect*

Results in the previous Section indicate a larger Joshi effect in the case of the aged gas than in a mixture of aged and fresh gas. It would then appear that ageing brings about an increase in the magnitude of the effect. The following experiments were designed to verify the above conclusion.

$\text{H}_2$  at a pressure of 80 mm. was aged *i.e.*, exposed to an applied potential of 5.5 kV, which was well above  $V_m$  of the system, for an hour. The discharge was stopped and immediately the potential variation of the system was studied. The gas was then allowed to stand for a short interval (3 hours) when another set of readings for the potential variation of the effect taken. Such sets of readings were taken at the end of various intervals for which the gas was allowed to stand. Now the pressure of the gas was lowered to the next desired value, *viz.*, 70 mm. and the above series of experiments repeated. The data thus obtained are reported in Table III and shown graphically in Fig. 2.

It is observed in general that ageing the gas under a large applied potential reduces the magnitude of the Joshi effect. On allowing the gas to stand for a few hours, it recovers from the effect of ageing and shows a larger Joshi effect. Thus for example, at a pressure of 80 mm. fresh  $\text{H}_2$  gives a maximum Joshi effect of 20.6% (*cf.* Table I).

TABLE III

*Influence of ageing on the relative Joshi effect in hydrogen.*

(a) Pressure of H <sub>2</sub> =80 mm.				(b) Pressure of H <sub>2</sub> =70 mm				(c) Pressure of H <sub>2</sub> =50 mm.						
kV.	<----->			At 500 cycles frequency	----->			At 500 cycles frequency	----->					
	After ageing for 1 hr at 5.5 kV.	After 4 hrs	After 16 hrs		After 24 hrs	Soon after previous study	After ageing for 1 hr. at 5.5 kV		After 16 hrs.	Soon after previous study	After ageing for 1 hr at 5.5 kV.	After 12 hrs. for 2 hrs.		
0.67	14.8	25.0	25.0	kV was varied 0.27 to 0.54 -%Δi varied between 4.8 & 0.5	22.5	19.6	kV was varied 0.27 to 0.54 -%Δi varied between 5.6 & 2.6	18.0	18.5	19.3	20.0	20.0	27.1	30.7
0.80	11.7	29.6	31.5		26.1	25.6		17.8	-	15.6	16.0	12.8	-	13.5
0.91	11.7	16.8	11.1		20.8	18.4		11.1	17.0	-	11.0		13.7	
1.07	8.8	14.8	14.3		12.8	15.5		9.5	15.8	10.1	10.2	10.1	11.6	8.9
1.20	7.7	11.8	10.1		10.1	9.7		7.3	9.3	8.5	8.1	6.7	7.9	7.4
1.31	6.4	8.4	8.6		8.0	7.6		5.6	7.0	4.1	4.8	5.0	5.8	4.2
1.47	1.9	5.2	6.4		5.2	6.2		4.6	5.4	2.8	4.1	3.9	4.0	3.0
1.60	0.6	1.1	4.0		1.3	1.0		2.6	3.1	-	3.0	3.2	3.2	2.8

On ageing it at 5.5 kV for 1 hour, the magnitude of the effect is reduced to 14.8% at  $V_m$ . The same is the case also at the higher potentials. When the gas is allowed to stand for 3 hours, the magnitude of the effect increases to 29.6% which is more than that given by even the fresh gas. An interval of 16 hours augments the value still further to 31.5%.

The influence of the frequency of the A.C. supply was incidentally studied by subjecting the gas of the previous experiments to applied potentials in the range of 0.27 to 0.54 kV of frequency of 500 cycles per second. Under these electrical conditions also, the system shows only negative Joshi effect; but its magnitude is considerably smaller than that for 50 cycles frequency and varies in the range of 4.8 to 0.5%. Results obtained for the potential variation of the gas once again at 50 cycles frequency, after allowing the gas to stand for 24 hours, show a diminution in the magnitude of the effect, viz., 26.1 which still is larger than that for the fresh gas.

A reduction in the pressure of the gas to the new value of 70 mm. is accompanied by a slight reduction in the Joshi effect as well. Exposure of the gas to potentials of 500 cycles frequency gives  $\% \Delta i$  varying in the range of 5.7 to 1.1, which again emphasises the striking contrast in the influence of the frequency difference on the production of the Joshi effect. When the gas is next exposed to 5.5 kV of 50 cycles frequency and immediately after, the potential variation of the Joshi effect studied, high values characteristic of the lower frequency are obtained for  $\% \Delta i$ . Allowing the gas to stand for 16 hours brings about, as before, an increase in the magnitude of the Joshi effect.

The above observations regarding the influence of ageing apply *in toto* to the case when the gas pressure is reduced to 50 mm.

In another series of experiments,  $H_2$  at 70 mm. was aged at an applied potential of 5.5 kV of 50 cycles frequency for half an hour, after which the potential variation of

Fig. 2

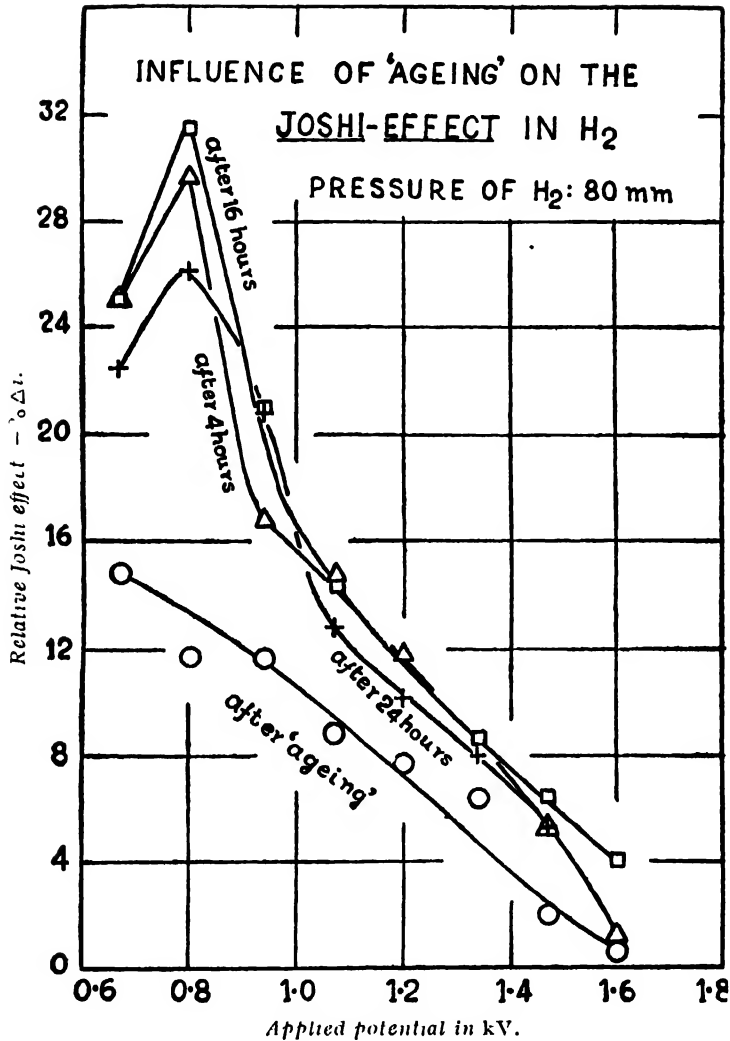


TABLE IV

*Influence of ageing on the potential variation of the Joshi effect.*

(a) Pressure of H<sub>2</sub> = 70 mm.

(b) Pressure of H<sub>2</sub> = 96 mm.

kV.	←----- -% Δi -----→						kV.	←----- -% Δi -----→		
	After ageing at 5.5 kV.	After 24 hours.	After 48 hours.	After 72 hours.	After 96 hours.	After 120 hours.		After ageing at 5.5 kV.	After 24 hours.	After 48 hours.
0.91	36.5	21.4	23.3	27.8	1.7	—	0.91	19.8	12.0	11.3
1.07	43.0	48.9	58.9?	45.7	4.0	—	1.07	43.1	23.5	29.7
1.23	42.9	22.2	21.2	29.2	4.1	—	1.23	—	—	—
1.33	17.8	14.5	12.8	14.7	1.7	2.4	1.33	31.1	13.2	9.3
1.49	17.6	15.4	12.1	8.3	1.3	2.5	1.49	18.0	—	—
1.60	—	—	—	4.8	—	1.8	1.60	17.5	—	—



the Joshi effect was observed in this gas. This was repeated at intervals of 24 hours during which the gas was allowed to stand. The pressure of the gas was then raised to 96 mm. by admitting fresh gas and observations similar to the above taken. Table IV contains some typical data obtained in the above series of experiments.

It is found, in general, that the magnitude of the effect in the gas allowed to stand for a prolonged period shows a progressive diminution. Thus,  $H_2$  at 70 mm. after a rest of 96 hours shows a large drop from 45.7 to 4.0%. The same feature is observed also in regard to the higher pressure studied, viz., 96 mm.

The above results lead to the conclusion that while allowing the gas to stand for moderate periods after ageing at a large applied potential results in improving the performance of the system with regard to the production of the Joshi effect, very large intervals extending into days exert a deleterious effect and the system loses its ability to show the Joshi effect to any marked extent. Such a behaviour of the gas points to an interaction between the gas and the electrode surface which may result in the formation of "a variable adsorption like boundary layer", photochemically active, as postulated by Joshi (*Curr. Sci.*, 1945, **14**, 175; 1947, **16**, 19) and which is the main seat of the phenomenon of the Joshi effect.

It is interesting to compare the influence of ageing observed in the present system with that in other systems. Deo (*Proc. Ind. Acad. Sci.*, 1945, **21A**, 76) found that in the case of an 'aged' ozoniser, that is, one which had been in use for work on the Joshi effect in  $Cl_2$  over one and half years showed no time variation of the effect, while in a fresh ozoniser  $i_0$  and  $i_1$ , as also  $\Delta i$  and  $\% \Delta i$ , increased considerably during a continued exposure to discharge. The 'ageing' effect in  $Cl_2$  was more pronounced under X-rays (Joshi, *Curr. Sci.*, 1944, **13**, 278) which produced a permanent decrease in the magnitude of the Joshi effect on exposing the ozoniser to the applied potential for half an hour. Goyal (this *Journal*, 1947, **24**, 203) found that in  $Cl_2$  'ageing' stabilises the discharge current, increasing markedly the Joshi effect over a wide range of applied potentials. Ramanamurti (*ibid.*, 1948, **25**, 255) has made kinetic studies of the progressive development of  $\Delta i$  during ageing and finds that it follows the equation for the 'first order' reactions. The results obtained for Hg vapour (B N. Prasad, unpublished results) are very striking in that the system initially gives no Joshi effect but develops it on ageing; the magnitude of the effect increases to a maximum on continued ageing, at which value it remains stationary thereafter.

It is suggested tentatively from a review of the results available for the influence of ageing on the production of the Joshi effect that easily adsorbed and reactive gases such as  $Cl_2$ ,  $Br_2$ ,  $I_2$ ,  $O_2$  and Hg develop or give a progressively increasing value of  $\% \Delta i$  reaching ultimately a maximum, while the 'permanent' gases such as  $H_2$ , air  $N_2$  etc., which undergo little adsorption, are not susceptible to 'ageing' influence to the same extent and in fact, lose the capacity to show the effect after prolonged ageing.

#### *Influence of Intensity of Incident Light*

That the Joshi effect is sensitive to changes in the intensity of irradiation has been observed in  $Cl_2$  (Joshi, *Curr. Sci.*, 1945, **14**, 35; Deo, *Indian J. Phys.*, 1944, **18**, 83).

In view of the observation of positive Joshi effect, *i. e.*, a photoincrease in the current in  $H_2$  (*loc. cit.*) and a number of other systems under certain conditions, a close connection between the photoelectric effect and the Joshi effect may be contemplated. It is known that in vacuum cells, photoelectric emission is strictly proportional to the intensity of light, while in gas-filled tubes subjected to electric fields, strong enough to produce ionisation by collision in the gas, the current may be expected to increase more than linearly with the intensity of irradiation. Hence it appeared instructive to study the influence of the intensity of the incident light on the magnitude of the Joshi effect.

Three different intensities of the irradiating light were obtained from three systems A, B, C of white incandescent bulbs in the following way. System A consisted of two 200-Watt bulbs and one 80-Watt bulb; B, of one 200-Watt bulb and one 80-Watt bulb; and C, of one 200-Watt bulb. These bulbs, rated for 220 volts, were worked at 180 volts which was kept constant by adjustment of a resistance in series. The actual intensities of the systems A, B and C were therefore in the ratio 307.2 : 179.2 : 128, *i. e.*, 2.4 : 1.4 : 1.

$H_2$  was admitted into the ozoniser at a pressure of 205 mm. and the potential variation of the Joshi effect of the system observed when the ozoniser was irradiated by the three systems of irradiation, one after the other. Two pressures of the gas were studied and the data obtained are shown in Table V.

TABLE V

*Influence of intensity of irradiation on the relative Joshi effect in hydrogen.*

kV.	205 mm. % $\Delta i$			156 mm. % $\Delta i$			107 mm. % $\Delta i$			75 mm. % $\Delta i$			55 mm. % $\Delta i$			40 mm. % $\Delta i$			30 mm. % $\Delta i$		
	A.	B.	C.	A.	B.	C.	A.	B.	C.	A.	B.	C.	A.	B.	C.	A.	B.	C.	A.	B.	C.
0.67										4.0	—	—	6.5	4.3	2.2	15.0	12.5	10.0	14.6	12.2	9.8
0.94										8.0	6.7	5.3	7.5	6.3	5.2	8.3	6.9	5.5	7.1	6.6	5.9
1.07							2.8	2.2	1.4	13.0	11.1	10.4	6.5	6.0	5.5	5.0	4.0	3.5	6.0	5.0	4.5
1.20				4.0	3.0	2.0	7.2	4.8	3.6	7.5	6.6	5.6	—	—	—	4.5	3.7	3.3	3.9	3.5	3.0
1.34				8.4	7.2	6.0	6.3	5.6	5.2	6.0	5.3	5.0	4.7	4.0	3.4	3.0	2.3	2.0	2.3	2.0	1.8
1.47	4.0	2.9	2.0	8.8	5.6	4.0	6.6	5.7	5.4	4.3	3.8	3.2	3.3	2.8	2.5	2.3	1.7	1.4	1.8	1.5	1.2
1.60	4.7	3.9	3.5	7.1	6.0	4.2	6.5	4.5	4.2	3.8	3.4	3.1	2.7	2.0	1.8	1.7	1.2	1.0	1.6	1.4	1.2
1.73	4.3	3.2	2.6	6.5	4.8	3.8	5.3	4.2	3.9	3.3	2.9	2.7	2.4	2.0	1.8	1.6	1.2	1.0	1.2	1.0	0.8
1.87	4.0	3.5	2.0	7.0	3.7	3.3	The relative intensities of the three sources of irradiation were in the ratio of A : B : C :: 2.4 : 1.4 : 1														
2.00	3.5	3.1	2.6																		
2.13	3.5	3.1	2.6																		

It is evident that the magnitude of the Joshi effect increases with the intensity of irradiation; but the variation is not linear. For low values % $\Delta i$  appears to be linear with the intensity of irradiation. But as % $\Delta i$  takes on higher values, its variation with the intensity of light becomes less than linear and tends to show saturation at higher intensities.

*Influence of Frequency of Incident Light*

Work on  $\text{Cl}_2$  has shown that the Joshi effect is markedly sensitive to the various spectral regions of the irradiating light and the magnitude of the effect for the different regions of same intensity is in the order : white  $>$  violet  $>$  green  $>$  red (Joshi, *Curr. Sci.*, 1945, **14**, 35, 317; Deo, *Science & Culture*, 1944, **9**, 252). Even when the red region had an appreciably larger intensity than violet,  $\% \Delta i$  was larger for violet than for green or red. Thus it appears that frequency and not intensity of the irradiating light is the more important determinant of the phenomenon. But since the light used viz., the violet band contains the region which is selectively absorbed by  $\text{Cl}_2$ , it could not be asserted without any ambiguity whether the Joshi effect is the result of selective absorption or frequency effect.  $\text{H}_2$ , unlike  $\text{Cl}_2$  and other gases, is known to be under ordinary conditions the most transparent gas. Even the very short waves, discovered by Schumann, which are powerfully absorbed by other gases, are freely transmitted by hydrogen. It appeared therefore interesting to study the role of frequency of the incident light in such a gas in regard to the production of the Joshi effect.

Different frequency regions of the irradiating light were obtained by the use of glass filters in front of the moving shutter of the box enclosing the bulbs. The transmission limits of the filters, as determined by a Hilger constant deviation spectrograph, were found to be as Violet, 4750 - 4000 Å; Green, 5775 - 5070 Å; Red, 7070 - 6070 Å; White, 7800 - 3700 Å.

$\text{H}_2$  was taken at pressures in the range of 50-20 mm. At each pressure the potential variation of the Joshi effect under irradiation of the ozoniser with the different frequency band was observed. Typical results selected out of several series of such data representing a wide range of exciting conditions are indicated in Table VI.

It is seen that at all applied potentials and pressures of the gas, the order of the magnitude of the Joshi effect is white  $>$  violet  $>$  green  $>$  red. In the last column under each pressure is given the sum total of  $\% \Delta i$  produced individually by the violet, green and red radiations. In every case the total exceeds the value for white light in spite of the fact that the range of frequencies transmitted by the three light filters is much less than that due to white light. This points to a saturation effect whereby the Joshi effect due to simultaneous irradiations in different spectral regions is less than the sum of the corresponding  $\% \Delta i$  produced separately.

The extreme transparency of  $\text{H}_2$  has been referred to. Hydrogen gas in the sun and stars shows strong absorption coincident with the emission lines seen when the gas is excited by electrical discharges in vacuum tubes. Attempts to reproduce these absorption lines in the laboratory have shown that absorption takes place only when the gas is in a state of luminiscence. Pfüger (*Ann. Physik*, 1907, **24**, 515) by exciting  $\text{H}_2$  at low pressure in a capillary tube by powerful electrical discharge from an induction coil and exposing  $\text{H}_2$ , contained in a large tube connected to the same electrical circuit, to the glow of hydrogen in the capillary tube was able to observe the red line distinctly reversed. Soon after, Ladenburg and Loria (*Verh. deutsch. phys. Ges.*, 1908, **10**, 858) using a similar arrangement reversed both the red and green lines. It is thus seen that hydrogen absorbs the  $\text{H}_\alpha$  and  $\text{H}_\beta$  lines only when it is power-

TABLE VI

*Influence of frequency of incident light on the relative Joshi effect.*

Applied potential	←----- % $\Delta i$ -----→				
kV.	White.	Violet.	Green.	Red.	Violet +green +red
Pressure of hydrogen = 50 mm.					
0.67	23.5	13.8	11.6	8.7	34.1
1.07	11.7	7.1	6.3	3.8	17.2
1.34	4.8	1.1	3.8	2.2	10.1
1.60	3.3	2.9	2.7	1.5	7.1
Pressure of hydrogen = 40 mm.					
0.67	29.3	16.0	15.1	9.7	40.8
1.07	12.8	7.5	7.0	4.4	18.9
1.34	5.4	1.0	3.1	2.2	9.6
1.60	3.6	2.8	2.5	1.6	6.9
Pressure of hydrogen = 30 mm.					
0.67	21.0	14.0	13.0	9.0	36.0
1.07	10.4	6.5	6.1	4.4	17.3
1.34	5.0	3.5	3.5	2.2	9.5
1.60	3.2	2.4	2.0	1.0	5.4
Pressure of hydrogen = 25 mm.					
0.67	21.3	15.6	13.9	10.0	39.5
1.07	12.0	6.3	5.8	1.5	16.6
1.34	1.3	3.3	3.0	2.3	5.6
1.60	2.6	2.1	1.8	1.3	5.2
Pressure of hydrogen = 20 mm.					
0.67	16.5	12.9	11.4	8.3	32.6
1.07	5.2	4.3	1.0	2.6	10.9
1.34	2.0	1.4	1.3	1.1	3.8
1.60	1.2	0.8	0.7	0.5	2.0

fully excited at low pressures. Lambrey and Chalonge (*Compt. rend.*, 1927, **184**, 1057) have observed that if potentials of 2 to 3 kV are applied to a tube containing  $H_2$  under 2.5 mm., a continuous spectrum is obtained extending from the red into the Schumann region. The  $H_\alpha$  ray is visible, but not the  $H_\beta$  or  $H_\gamma$  rays. The spectrum is stable for at least 5 minutes.

Now, in the present experiments,  $H_2$  was taken at comparatively very high pressures, viz., 20 to 50 mm. and excited at potentials intended to give large values of the Joshi

effect ; hence the applied potentials were not far removed from  $V_m$ . In these circumstances,  $H_2$  will not be in a condition to show selective absorption. The occurrence of the Joshi effect under all frequencies of the irradiating light and especially the magnitude of the effect being in the order : violet > green > red, makes it clear that the effect is *not* the result of selective absorption but is a frequency or quantum phenomenon and that of the two factors, intensity and frequency which influence the magnitude of the effect, the latter is the more important determinant.

#### *Influence of Temperature*

It is known that the photoelectric effect is not influenced by temperature. Since the Joshi effect also is a photo-phenomenon, it is of interest to investigate the influence of temperature on its production.

For experiments reported in this Section, the ozoniser was enclosed in a box lined with asbestos internally and heated electrically by means of coils of resistance wire fixed along the walls of the box. On the outer and inner electrolytes showing a steady temperature at the required value, studies of the potential variation of the Joshi effect were carried out. The range of temperature investigated was from  $15^\circ$  to  $55^\circ$ . The room temperature was  $30^\circ$ ; after a study had been made at a different temperature, readings for the potential variations of the Joshi effect were taken at the room temperature. Such a procedure helped to disentangle any effect due to 'ageing' from that due to temperature variation. The data are given in Table VII (cf., Fig 3). The temperatures are indicated in the order in which they were varied.

TABLE VII

*Influence of temperature on the relative Joshi effect.*

Applied potential kV.	Pressure of hydrogen = 90 mm							
	— % $\Delta I$ at temperature —————>							
	$30^\circ$ .	$47^\circ$ .	$30^\circ$ .	$55^\circ$ .	$30^\circ$	$20^\circ$ .	$30^\circ$	$15^\circ$ .
0.54	—	—	—	—	7.0	1.7	11.1	14.1
0.80	6.5	6.8	7.1	6.2	14.2	18.3	19.1	23.3
0.91	5.2	7.3	15.9	12.7	23.7	24.9	17.8	24.6
1.07	17.1	15.9	17.0	14.0	17.9	17.9	16.0	15.9
1.17	17.0	13.3	17.5	12.8	13.9	14.4	13.5	13.3
1.28	13.3	10.7	12.2	7.1	13.2	11.7	11.7	12.1
1.33	11.1	9.2	10.6	6.9	11.8	11.9	12.5	10.8
1.39	9.7	7.0	9.7	6.3	—	9.6	10.7	10.2
1.44	9.8	7.6	9.1	5.5	9.4	9.7	9.1	9.5
1.49	10.0	—	—	—	—	—	—	—

In general it is found that with increase of temperature,  $\% \Delta i$  shows an appreciable diminution in value. For example, at 0.80 kV, the values of  $\% \Delta i$  at 30°, 47°, 55°, 20° and 15° are 6.5, 6.8, 6.2, 18.3 and 23.3 respectively, while at a higher potential, say 1.33 kV, they are 11.1, 9.2, 6.9, 11.9 and 10.8 respectively. The values of  $\% \Delta i$  obtained at the room temperature immediately after a set of readings had been taken at a different temperature are seen to be not quite constant for any definite potential. This is especially so at lower potentials. This is to be attributed to the effect of ageing which thus seems to affect the magnitude of the Joshi effect more at lower than at higher potentials.

Since the Joshi effect is found to be maximum at/near  $V_m$  and diminishes as  $V$  increases, it may be inferred from the fact that  $\% \Delta i$  at a particular potential decreases as the temperature increases, that  $V_m$  of the system decreases and hence the effective applied potential ( $V - V_m$ ) increases with increase of temperature. This may be brought about in two ways, viz., (a) the electronic velocity may increase, or/and (b) the conductivity of the glass walls of the ozoniser may increase at higher temperatures. But it is known that the electronic mobility is independent of temperature. If the conductivity of the glass walls increases appreciably with temperature, an increase in the current  $i_b$  at constant applied potential may be expected. But it is seen from Table VIII, where the currents  $i_b$  corresponding to various applied potentials at the different temperatures are given, that over the range of temperatures studied, viz., 15° to 55°,  $i_b$  remains nearly constant. This is more apparent at the higher than at the lower potentials where the ageing effect interferes with the constancy of  $i_b$ . Thus, temperature is found to have no influence on  $i_b$  but affects  $i_L$  in such a way that a decrease in the net and relative Joshi effect results with increase of temperature. This points to some sort of a conditioned surface capable of responding to the incident light.

TABLE VIII

*Discharge current at different temperatures.*

Applied potential kV.	Pressure of hydrogen = 90 mm.							
	Discharge current in milliamps at							
	30°.	47°.	30°.	55°.	30°.	20°.	30°.	15°.
0.54	0.010	0.010	0.015	0.020	0.025	0.025	0.025	0.025
0.80	.025	.025	.025	.035	.040	.040	.050	.050
0.91	.055	.055	.070	.070	.090	.085	.085	.085
1.07	.130	.130	.130	.140	.130	.130	.130	.125
1.17	.165	.165	.160	.170	.160	.155	.160	.150
1.28	.190	.195	.195	.200	.190	.180	.195	.180
1.33	.210	.210	.210	.220	.200	.200	.210	.200
1.39	.230	.230	.225	.235	—	.210	.225	.215
1.44	.250	.250	.245	.255	.225	.225	.240	.230

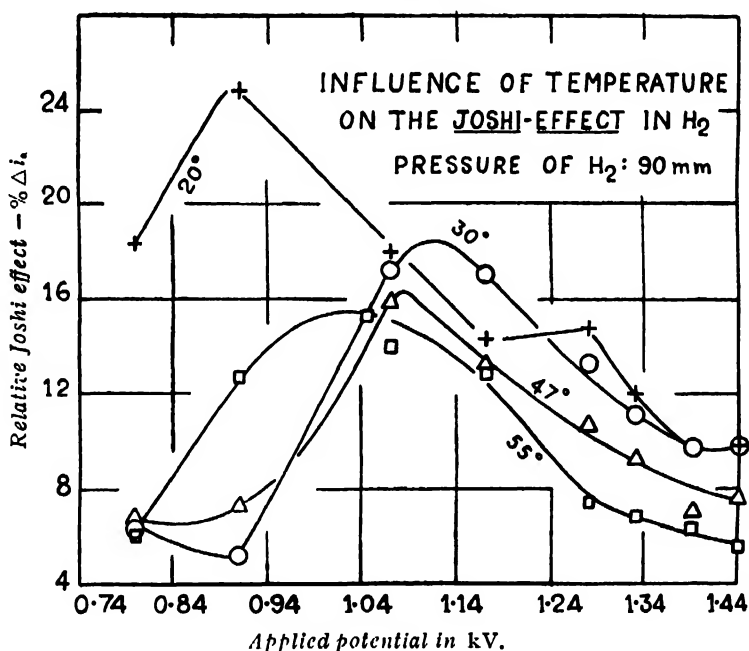
Numerous workers have shown that the classical photoelectric effect is not influenced by temperature changes; the temperature has been varied from -190° to 800°. But great care had to be taken to keep the photoelectric surface absolutely clean and

outgassed by heating. Ladenburg (*Verh. deutsch. phys. Ges.*, 1907, 9, 165) found that in the best vacuum attainable in his time, fresh surfaces of metals did show a slight temperature effect, but this disappeared on outgassing. Hence the production of the Joshi effect only in the presence of the gas and its dependence on the temperature is of significance for an elucidation of its mechanism.

A critical examination of Joshi's theory of the phenomenon (*Proc. Indian Sci. Cong.* 1946, *Phys. Sec.*, Abst. No. 25 ; *Curr. Sci.*, 1947, 16, 19) in the light of the foregoing results for  $H_2$  may now be attempted.

The theory contemplates three stages, viz., (a) formation of a boundary layer on the container walls derived in part from adsorption of ions and molecules under applied fields intense enough to cause dielectric breakdown of the gas; (b) photoelectric emission of electrons from this boundary layer under external irradiation, and (c) capture of these photoelectrons by the excited neutral molecules and atoms on account of their electron affinity to form negative ions of low mobility, resulting in current diminution as a space charge effect.

FIG. 3



The discharge space under potentials causing ionisation by collision abounds in various species of particles such as normal and excited atoms and molecules of the gas, positive and negative ions, electrons etc. Destruction of metastable atoms and recombination of ions on irradiation were originally suggested by Joshi as probable factors in the production of the effect. The observation of a large  $\% \Delta i$  in  $H_2$  observed in the present investigation, which according to Loeb ("Fundamental Processes of Electrical Discharge in Gases", p. 496) "gives a fairly low value of  $V_s$  (starting potential) and has no metastables" rules out the possibility of the effect being due to destruction of the metastables on irradiation. As regards the other suggestion, there is no instance

available in the literature where recombination of ions under irradiation has been observed. Further, if recombination were to occur under light, a spectral shift in the intensity or frequency of the glow in the discharge may be expected to follow. No such change has been observed so far.

The present theory of the *effect* advanced by Joshi, and outlined above, would appear to explain satisfactorily all the various features observed. Thus, the absence of the *effect* under potentials less than  $V_m$ , coupled with its development in an 'ageing' ozoniser and its diminution at higher temperatures supports Joshi's first postulate viz., formation of an adsorption-like boundary layer between the glass wall and the excited gas. The profound influence of the frequency and to a less extent, the intensity of the irradiating light on the *effect* establishes the photoelectric nature of the adsorbed layer. The observation of a large positive *effect* i. e., photoincrease of current under certain conditions, generally just below  $V_m$  of the system, may be cited as an additional evidence. It is well known that photoelectric currents from glass surface are very feeble. Whencit and Schmerwitz (*Z. Physik*, 1929, **57**, 533) found that even when the full light from a carbon arc was allowed to fall on the surface of a glass plate  $18 \times 18 \times 0.13$  mm., the currents were feeble, being of the order of  $10^{-13}$  amp. Since the ionisation potentials of gases are well above 10 volts, their photoelectric threshold is shorter than  $1234 \text{ \AA}$ , and they can show no photoelectric effect under visible light. Hence, the production of the Joshi effect under visible light including the red end of the spectrum leads to the conclusion that the work function of the 'boundary layer' postulated by Joshi should be low.

The author takes this opportunity to express his grateful thanks to Prof. S. S. Joshi, D. Sc., F. R. I. C., F. N. I., University Professor and Head of the Chemistry Department, for his kind interest and valuable guidance and discussions during the progress of these investigations.

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# DIELECTRIC CONSTANT AND DIPOLE MOMENT OF SOME DRUGS. PART I

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The dielectric constant of salantonin, barbitones, phenacetin, acetanilide and acetylsalicylic acid has been for the first time determined and the moments have been calculated by applying the new equation. The moment of *L*-ascorbic acid has been recalculated.

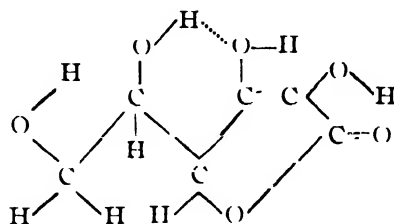
Dipole moment of *l*-ascorbic acid in dioxane solution has been studied by Kumler (*J. Amer. Chem. Soc.*, 1940, **62**, 292); the results have been recalculated by applying the new equation developed by Jatkar, Sathe and Iyengar (*J. Ind. Inst. Sci.*, 1946, **28A**, Part II, pp. 1-15)

TABLE I

$w_2$	$\epsilon$	$d$	$P_2$	$\mu \times 10^{18}$
Solvent = dioxane. Temp. = 25°. $P_1 = 152.8$				
0.0000	2.21366	1.0280	—	—
0.003955	2.25919	1.0.996	2079.6	3.22
0.006030	2.28458	1.03070	2126.3	3.25
0.009054	2.32136	1.03218	2342.0	3.28

The symbols used in the tables are :  $w_2$ , wt. fraction of the solute ;  $d$ , the density of the solution ;  $P_2$ , the polarisation of the solute ;  $P_F$ , the electronic polarisation of the solute ;  $\epsilon$ , the dielectric constant ;  $\mu$ , the dipole moment (cf. Kumler, *loc. cit.*).

The new value of moment is 3.25 as against the D. C. M. value 3.93D. Kumler has proposed the structure

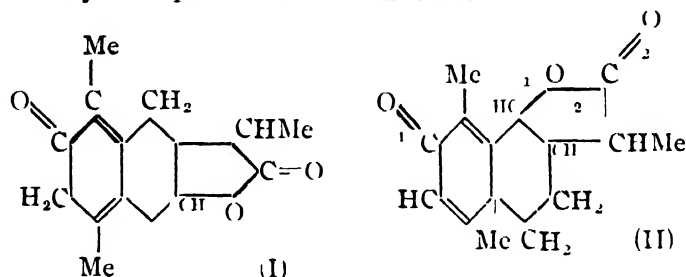


with an intramolecular hydrogen bonding. It is not possible to prepare a model of this compound as there is a considerable strain in the pentacyclic unsaturated ring and hence it is not possible to explain the dipole moment.

*Santonin*

The chemistry of santonin was investigated by Cannizaro *et al* (cf. Clemons, *J. Chem. Soc.*, 1929, 2368) and various constitutional formulae have been suggested of which

structure (I) was proposed by Grassi-Cristaldi (cf. Gucci and Grassi-Cristaldi, *Gazzetta*, 1892, 22, 1) and structure (II) by Clemono *et al* (*J. Chem. Soc.*, 1930, 2579) after direct synthesis of *dl*-santonous acid and racemic desmotropo-santonin. No previous work has been done to study the dipole moment of santonin.



The dielectric constant of santonin was measured in benzene solution at 3 concentrations and two temperatures. The results are given below.

TABLE II

$w_2$	$\epsilon_s$	$d$	$P_2$	$\mu \times 10^{18}$
Solvent = benzene. Temp. = 21°				
0.00503	2.3270	0.8934	3531	1.14
0.02002	2.6250	0.8785	5192	5.10
0.02614	2.7990	0.8823	5811	5.40
Solvent = Benzene. Temp. = 12°				
0.00503	2.2970	0.8576	3300	1.11
0.02002	2.5788	0.8617	4975	5.10
0.02614	2.7286	0.8621	5523	5.13

There is an unusually marked effect of concentration on the dipole moment. The moment of santonin in benzene solution varies with concentration, the infinite dilution value being 3.7D. This value supports structure (II). The two C=O groups are nearly at an angle of 120 degrees in (II) and 150° in (I). Calculating the components along the two polarisable groups C=O in (II), the moment along  $\text{C}=\text{O} = [3.0 (\text{C}-\text{O}) + 1/8 (3.0 (\text{C}=\text{O}) + 1.8 (\text{C}-\text{O}) - 1/2 \times 1.8 (\text{C}-\text{O}))] = 3.5$  and along  $\text{C}=\text{O} = 3.0 (\text{C}-\text{O}) - 1/8 [3.0 (\text{C}=\text{O}) + 1.8 (\text{C}-\text{O}) - 1/2 (\text{C}-\text{O})] = 3.5$  D. The hydrocarbon groups contribute the balance of 0.2D.

#### Barbitone

No previous work has been reported on the dielectric constant of barbitone and phenobarbitone. In the present paper the moments of these compounds in dioxane solution have been studied.

TABLE III

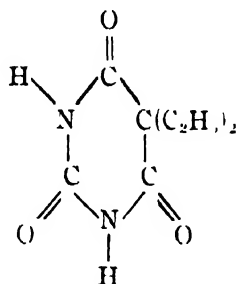
$w_2$	$\epsilon$	$d$	$P_2$	$\mu \times 10^{18}$
Barbitone : Solvent = dioxane. Temp. = 25°. $P_1 = 190.5$				
0.0887	2.2622	1.0466	411.6	1.10
0.0835	2.2556	1.0468	411.6	1.10
0.0725	2.2477	1.0433	441.3	1.10
Phenobarbitone : Solvent = dioxane. Temp. = 25°. $P_1 = 228.4$				
0.1037	2.2808	1.0557	498.4	1.20
0.0703	2.2477	1.0433	411.3	1.16

TABLE IV

Temp.	$w_2$	$\epsilon$	$d$	$P_2$	$\mu \times 10^{18}$
1. Acetanilide : Solvent = benzene. $P_1 = 150$ .					
22°	0.0103	2.432	0.8761	2495	3.55
44°	"	2.373	0.8592	2028	3.55
Solvent = dioxane.					
23°	0.07128	3.616	1.038	2835	3.78
40°	"	3.497	1.023	2656	3.76
2. Phenacetin : Pure (molten) liquid $P_E = 200$ .					
Temp.		$\epsilon$	$d$	$P_1$	
165°		24.157	1.008	4117.0	5.56
150°		25.848	1.017	4375.0	5.64
135°		27.985	1.027	4707.0	5.75
Solvent = dioxane.					
	$w_2$	$\epsilon$	$d$	$P_2$	
25°	0.0180	2.681	1.0311	5373	5.30
35°	"	2.671	1.0219	5377	5.35
3. Acetylsalicylic acid : Solvent = dioxane Temp. = 25°. $P_E = 179.6$ .					
$w_2$		$\epsilon$	$d$	$P_2$	
0.0255		2.2583	1.0351	802.4	2.07
0.0673		2.473	1.044	1017.0	2.11
Solvent = dioxane. Temp. = 35°.					
0.0255		2.2470	1.027	719.8	2.00
0.0673		2.426	1.031	910.3	2.02

(The variation of moment 1.16–1.20D in the case of phenobarbitone is within the limit of experimental error).

The results show that there is no concentration effect and that the moments of both are nearly the same (1.10) as expected. The small moment is in harmony with a symmetrical structure of barbitone.



*Acetanilide, Phenacetin, Acetylsalicylic Acid*

There is no previous work on the dipole moment of antipyretics. The author has investigated the dielectric constant and dipole moment of acetanilide,  $C_6H_5NHC(=O)CH_3$ , in dioxane and benzene, of phenacetin  $C_2H_5OC_6H_4NHC(=O)CH_3$  in pure molten state as well as in dioxane solution and of acetylsalicylic acid,  $C_6H_4(COOH)OCOCH_3$  in dioxane solution. The dipole moments are calculated by applying the new relationship. The results are shown in Table IV.

The high moment of acetanilide is obviously due to NH group which has a high ionic character (78%). The acetyl group gives a positive component to NH bond when calculated along the connecting links and *vice versa*. The moment along  $C=O$ , the most polarisable group, comes to 3.4 as compared to 5.6 observed (average value from the data on benzene and dioxane).

The moment of phenacetin is abnormally high and may be due to resonance.

The comparatively low moment of acetylsalicylic acid indicates internal hydrogen bonding.

Thanks of the author are due to Dr. S. K. K. Jatkari for guidance and to the Council of Scientific & Industrial Research for the financial help during this research.

# DIELECTRIC CONSTANT AND DIPOLE MOMENT OF SOME DRUGS PART II

(Miss) S. B. KULKARNI

Dielectric constant of sulphanilamide has been determined in dioxane and the dipole moment calculated by applying the new equation. The moments of compounds related to sulphanilamide have been recalculated from the literature data and the moments discussed in the light of their structure.

The study of the dielectric properties of the sulfa drugs is very interesting from the point of view of their pharmacological properties. Unfortunately these drugs have been found to be high melting and insoluble in organic solvents. The dielectric constant of sulphanilamide, which is soluble in dioxane, has been investigated and the dipole moment calculated by applying the new equation of Jatkar *et al.* (*J. Ind. Inst. Sci.*, 1946, **28A**, Part II). The previous data on the dipole moment of sulphanilamide and related compounds have been also recalculated. The results are given in the following table.

TABLE I

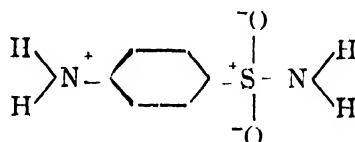
		$d$ .	$P_2$	$\mu \times 10^{18}$ .	$\mu_D$
1. Benzene sulphonamide Solvent = dioxane at 25°. $P_1 = 156$ .					
0.001210	2.2987	1.0288	3393	4.17	5.09
0.008237	2.3386	1.0287	3426	4.19	
0.012669	2.4694	1.0295	3452	4.20	
0.015631	2.5460	1.0311	3433	4.19	
2. <i>p</i> -Phenylbenzene sulphonamide Solvent = dioxane at 25°. $P_1 = 262$					
0.004831	2.2831	1.0286	3740	4.32	5.2
0.008125	2.3338	1.0287	3717	4.30	
0.011312	2.3835	1.0295	3717	4.30	
0.016929	2.4697	1.0311	3689	4.28	
3. Sulphanilamide Solvent = dioxane at 25°. $P_1 = 180$ .					
0.004368	2.3496	1.0281	5556	5.37	6.63
0.007848	2.4635	1.0296	5552	5.37	
0.010880	2.5629	1.0305	5557	5.38	
0.017019	2.7681	1.0327	5620	5.40	
* { 0.009798	2.9189	1.0331	5575	5.40	
{ „ (40°)	2.8292	1.0157	5062.5	5.35	
4. ( <i>p</i> -Aminophenyl) benzene sulphanilamide Solvent = dioxane at 25°. $P_1 = 230$ .					
0.002465	2.2692	1.0276	6130	5.59	6.73
0.003828	2.3020	1.0281	6124	5.59	
0.006156	2.3597	1.0284	6137	5.59	
0.007888	2.4037	1.0291	6175	5.61	

## DISCUSSION

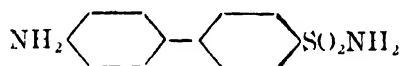
Kumler *et al.* (*loc. cit.*) have calculated the moment of sulphanilamide by making use of the formula for free rotation,

$$\mu_{\text{r}} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta \cos C_1 \cos C_2} \quad \dots (1)$$

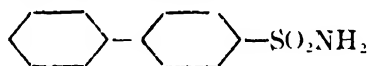
where  $\mu_1$  is the moment of amine group,  $\mu_2$ , the moment of sulphonamide group,  $\theta$ , the angle between the axis of rotation, and  $C_1$  and  $C_2$ , the angles which the two moments make with their respective axis of rotation. The calculated moment by applying this formula is 5.82 which is less than the observed Debye's value of moment 6.63, and hence he postulated about 3% contribution of the resonance structure



According to Kumler the therapeutic effects of sulphanilamide and related compounds are associated with the contribution made by the forms with a separation of charges. The recalculated values of moments are 4.10 for benzene sulphonamide ( $\text{C}_6\text{H}_5\text{SO}_2\text{NH}_2$ ) and 1.5 for aniline and 5.4 for sulphanilamide ( $\text{H}_2\text{NC}_6\text{H}_4\text{SO}_2\text{NH}_2$ ), which is 0.3 less than the sum of aniline and sulphonamide. Similarly, the recalculated moment 5.6 of the compound *p*-phenylbenzene sulphanilamide



is 0.2 less than the sum of the moments of the corresponding *p*-phenylbenzene sulphonamide



(4.3D) and aniline. These differences are considerably less than the discrepancies (0.8) given by the equation (1) and also those calculated by the addition of the D.C.M. moments of aniline (1.9) and benzene sulphonamide (5.1) the sum of which is more than the D.C.M. moment 6.6 for sulphanilamide which result cannot be explained by the concept of resonance.

The application of the new equation clears away the whole difficulty and the observed moment is nearly equal to the sum of the individual moments.

Thanks of the author are due to Dr. S. K. K. Jatkari for guidance and to the Council of Scientific and Industrial Research for the financial help during this research.

# DIELECTRIC CONSTANT AND DIPOLE MOMENT OF SOME DRUGS. PART III

By (Miss) S. B. KULKARNI

The dielectric constant of 8-hydroxyquinoline in pure molten state, as well as in solutions, and of 4 different 5:7-chloro-iodo substituted 8-hydroxyquinoline derivatives in benzene solution has been determined and the dipole moments calculated by applying the new equation. The compound 5:7-di-iodo-8-hydroxyquinoline, which is reported to be most toxic, has highest dipole moment, 6.36D.

A number of chlorine- and iodine-substituted derivatives of 8-hydroxyquinoline have been reported to be very useful as internal antiseptics for amoebic infection (cf. Leake, *J. Amer. Med. Assoc.*, 1914, **98**, 106). The activity of these drugs is believed to be due to the liberation of iodine in the intestine. In order to find out the relation, if any, between the activity and dipole moment, the author has investigated the dipole moment of four isomeric chloro-iodo-8-hydroxyquinolines which were kindly supplied by Dr. T. N. Ghosh of the Bengal Immunity Research Laboratory, Calcutta. The dielectric constant of 8-hydroxyquinoline in pure molten state as well as in benzene and carbon tetrachloride solution has been determined for the first time and the dipole moments are calculated by applying the new equation of Jitkar *et al.* (*J. Ind. Inst. Sci.*, 1946, **28A**, Part II). The results are presented in the following tables.

TABLE I

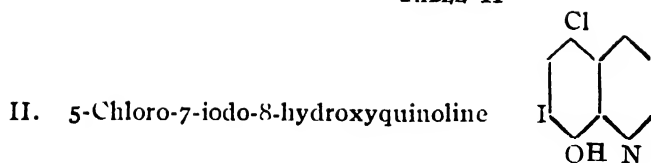


I. 8-Hydroxyquinoline.

$$P_1 = 168.5$$

Temp	$\epsilon$	$d$	$P$	$\mu \times 10^{18}$	
1. Molten liquid :					
120°	8.052	1.135	0.016	2.28	
100°	8.287	1.150	0.116	2.28	
22°	3.126	---	---	---	
$f_d$	$\epsilon$	$d$	$P_2$	$\mu \times 10^{18}$	$\mu D$
2. Solvent = benzene. Temp. = 25°					
0.1029	2.8669	0.8987	1081.1	2.21	2.52
0.1315	3.0513	0.9073	1098.6	2.23	
Solvent = benzene. Temp. = 10°.					
0.1029	2.8282	0.8843	1067.1	2.25	
0.1315	2.9832	0.8931	1050.5	2.23	
3. Solvent = CCl <sub>4</sub> . Temp. = 25°.					
0.0318	2.5453	1.5492	1070	2.21	
0.0371	2.6129	1.5606	1130	2.27	
0.0485	2.7372	1.5581	1132	2.27	
Solvent = CCl <sub>4</sub> . Temp. = 40°.					
0.0371	2.4959	1.5423	981	2.20	
0.0485	2.7139	1.5373	1132	2.31	

TABLE II



$f_2$	Temp	$\epsilon$	$d$	$P_2$	$\mu \times 10^{18}$	$\mu_1$
0.002531	18.5°	2.3074	0.8839	1147.5	2.14	2.1
"	48°	2.2513	0.8565	983.5	2.03	
III. 5-Iodo-7-chloro-8-hydroxyquinoline $P_F = 271.9$						
0.001120	19.5°	2.3023	0.8806	2014.4	3.11	
"	45°	2.2669	0.8565	1898.5	3.35	3.4
IV. 5:7-Dichloro-8-hydroxyquinoline $P_F = 236.3$						
0.001484	22°	2.3288	0.8763	3165.3	4.16	
"	40°	2.3063	0.8600	3548.5	4.31	5.9
V. 5:7-Di-iodo-8-hydroxyquinoline. $P_1 = 30.4$						
0.000519	20°	2.3232	0.8787	7989.7	6.36	
"	46°	2.2838	0.8519	7351.4	6.30	7.5

TABLE III

Table of moments.

Substance.	Solvent.	Temp.	$\mu \times 10^{18}$	$\mu_D$
1. 8-Hydroxyquinoline (8 H Q)	Pure liquid	100°-120°	2.28	
"	C <sub>6</sub> H <sub>6</sub>	25°-40°	2.23	2.52
"	CCl <sub>4</sub>	25°, 40°	2.23	
2. 7-Chloro-7-iodo-8H.Q	C <sub>6</sub> H <sub>6</sub>	18.5°, 40°	2.10	2.4
3. 5-Iodo-7-chloro-	"	19.5°, 40°	3.33	3.4
4. 5:7-Dichloro-	"	22°, 40°	4.23	5.9
5. 5:7-Di-iodo	"	20°, 46°	6.36	7.5

## DISCUSSION

In the 5:7-substituted 8-hydroxyquinolines, the 5-chloro-7-iodo- compound, which is known as 'Vioform' has the lowest moment (2.1), the moment of 5-iodo-7-chloro being 3.2D and that of 5:7-dichloro (4.2) and 5:7-di-iodo-8-hydroxyquinoline having the highest (6.36) moment. Some chemical tests indicate that the iodine atom in 5-iodo-7-chloro-8-hydroxyquinoline ( $\mu=3.26$ ) is more strongly bound than that in vioform i.e., 5-chloro-7-iodo-8-hydroxyquinoline ( $\mu=2.1$ ) (Ghosh *et al*, *J. Indian Chem Soc.*, 1944, **21**, 352) and as such the former compound is expected to liberate iodine more slowly than vioform in the system and thus may exert a more sustained therapeutic activity in the treatment of amoebiasis. However, no pharmacological data have been reported as yet.

5:7-Di-iodo-8-hydroxyquinoline is reported to be most toxic of these series of compounds, which has also the highest dipole moment. The 5:7-dichloro compound has not been investigated for its pharmacological properties. The moments calculated by applying Debyes' equation ( $\mu_D$ ) are systematically higher than the new values.

Thanks of the author are due to Dr. S. K. K. Jatkar for guidance and to the Council of Scientific & Industrial Research for the financial help during this research.



## DIELECTRIC CONSTANT AND DIPOLE MOMENT OF DDT

BY (MISS) S. B. KULKARNI

Commercial DDT was purified by recrystallising from absolute alcohol, the melting point of pure compound being 108.5-109°. The dipole moment of *p*:*p'*-DDT in pure molten state as well as in benzene, carbon tetrachloride and dioxane solutions were determined and explained as due to free rotation of the groups along different bonds. The dehydrochlorinated product, *p*:*p'*-(ClC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C=CCl<sub>2</sub> being a symmetrical compound is shown to be nonpolar. The dipole moments of the compounds related to DDT have also been recalculated by applying the new equation. The toxicity of the *o*:*p'*-, *m*:*p'*- and *p*:*p'*-DDT has been calculated by applying the law of mass action and it has been shown that the log of mortality coefficient (*K*) varies linearly with the dipole moment, *p*:*p'*-DDT with lowest moment (1.1D) being the most toxic compound in this series.

The discovery by Muller (Swiss Patent, 226180, 1910) of the remarkable insecticidal properties of DDT has created great interest. This product is obtained by condensation of chloral (its alcoholate or hydrate) with chlorobenzene, and consists essentially of a mixture of two isomers, 1-trichloro-2:2-bis-(*p*-chlorophenyl)-ethane, called *p*:*p'*-DDT and trichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane (called *o*:*p'*-DDT) together with minor constituents of *o*:*o'*-DDT (West and Campbell, *Chem. Ind.*, 1945, **20**, 154). Studies leading to the discovery of DDT as an insecticide were first presented by Lauger, Martin and Müller (*Helv. Chim. Acta*, 1944, **27**, 892). The insecticidal properties of DDT and its related compounds have been reviewed in great detail by Haller (*J. Amer. Chem. Soc.*, 1945, **67**, 1561; *Ind. Eng. Chem.*, 1945, **39**, 467).

Although DDT is chemically unreactive and stable to long boiling with water, it readily loses hydrochloric acid to alcoholic alkali on mere boiling to form *p*:*p'*-bis-4-chlorophenyl-(1:1)-dichloroethane, *p*:*p'*-(ClC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C=CCl<sub>2</sub>. This compound as well as 4:4'-dichlorobenzophenone and bis-(4-chlorophenyl)-acetic acid are almost inactive both as stomach and contact poisons. According to Martin and Wein (*Nature*, 1944, **154**, 512) the toxicity of *p*:*p'*-DDT is due to its chemisorption at vital centres by interferences with essential enzyme system after intercellular decomposition to form hydrochloric acid and the ethylene derivative. As the ethylene derivative is nontoxic, the toxicity is ascribed to the hydrogen chloride. Diphenyltrichloroethane also readily loses hydrochloric acid in presence of alkali, yet it is relatively nontoxic. An additional factor, *lipoid solubility* of the molecule, as a whole, is therefore operative. The chlorophenyl group of the DDT is highly *lipoid soluble*.

We have studied the dielectric properties of DDT and related compounds with a view to correlating their insecticidal properties with the electric moments.

### EXPERIMENTAL

The commercial DDT melts over a wide range of temperature as it contains different isomers and related compounds. The commercial DDT was recrystallised twice from absolute alcohol, melting point of the product obtained was 108.5°-109°, in agreement with the value reported by Haller *et al* (*loc. cit.*). The mother-liquor contained *o*:*p'*-DDT. *p*:*p'*-DDT on boiling with ethanolic potassium hydroxide gave dehydrochlorinated product, 1:1-dichloro-2:2-bis-(*p*-chlorophenyl)-ethylene, m.p. at 88-89°.

DDT is relatively unstable at temperatures above 120° and in presence of metallic

salts (Martin *et al.*, *loc. cit.*). Molten DDT was found to decompose in presence of finely divided carbon.

The dipole moments of DDT in pure molten form, as well as in benzene and carbon tetrachloride solution, and also of dehydrochlorinated DDT were determined by the present author (*Proc. Indian Sci. Cong.*, 1945, Part III, *Chem. Sec.*, Abst. No. 33). The dipole moments of 12 derivatives of diphenyltrichloroethane were determined by Wild (*Helv. Chim. Acta*, 1944, **27**, 892). These results have been recalculated by employing the new equation (Jatkar *et al.*, *J. Ind. Inst. Sci.*, 1946, **28A**, Part II).

$$P = \frac{(\epsilon - 1)M}{d}; P_1 = \frac{(n^2 - 1)M}{d} \text{ and}$$

$$P - P_r = \frac{4\pi N \mu^2}{kT} \text{ for pure liquid and}$$

$$P_{12} = \frac{(\epsilon - 1)(M_1 f_1 + M_2 f_2)}{d_{12}} = P_1 f_1 + P_2 f_2 \text{ and } P_2 - P_1 = \frac{4\pi N \mu^2}{kT}$$

for solutions.

The corresponding electronic polarisation was calculated from the atomic refraction [cf. Kucken and Wolf, "Hand und Jahrbuch der chemisch physik", 1935, (6), A-B] The results are shown in the following table.

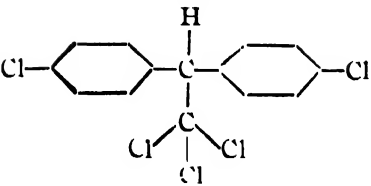
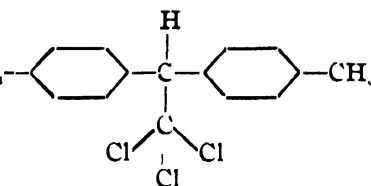
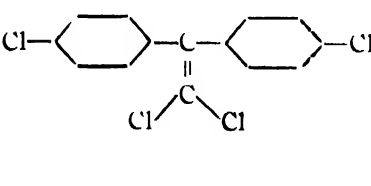
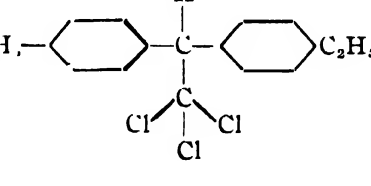
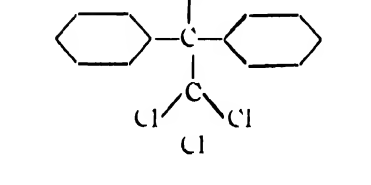
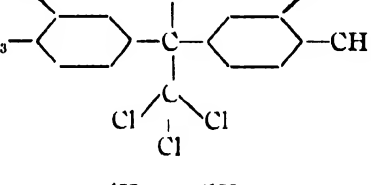
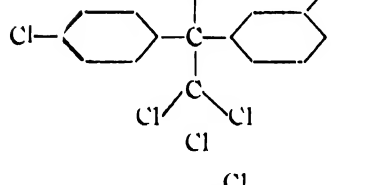
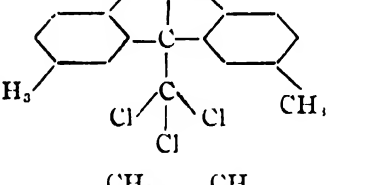
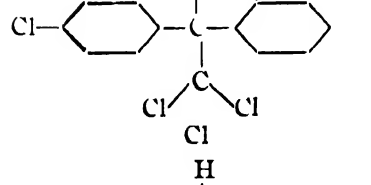
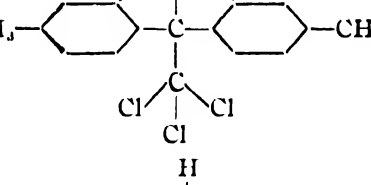
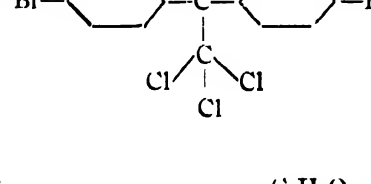
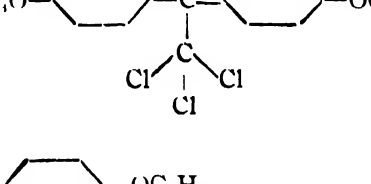

TABLE I

1. <i>p</i> -DDT (a). Pure liquid $P_1 = 335.9$				
Temp.	<i>d.</i>	$\epsilon$ .	$P_1$ .	$\mu \times 10^{18}$ .
145°	1.348	2.381	481.2	1.05
130°	1.361	2.852	481.6	1.03
110°	1.380	2.884	490.3	1.03
104°	1.388	2.900	485.0	1.00
Solvent = CCl <sub>4</sub> Temp. = 25° (a).				
$f_2$ .	<i>d.</i>	$\epsilon$ .	$P_2$ .	$\mu \times 10^{18}$ .
0.05888	1.545	2.393	631.7	1.12
Solvent = dioxane. Temp. = 25° (a).				
$w_2$ .	<i>d.</i>	$\epsilon$ .	$P_2$ .	$\mu \times 10^{18}$ .
0.1115	1.0633	2.2614	644	1.19
Solvent = benzene. Temp. = 20° (b)				
$f_2$ .	<i>d.</i>	$\epsilon$ .	$P_2$ .	$\mu \times 10^{18}$ .
0.00201	0.8778	2.2875	566.119	1.11
0.00506	0.8825	2.2963	571.877	1.11
0.01023	0.8910	2.3080	538.798	1.03
0.01551	0.8990	2.3205	536.828	1.03
2. Dehydrochlorinated DDT : Solvent = benzene. Temp. = 27° (a). $P_r = 287$ .				
$f_2$	<i>d.</i>	$\epsilon$ .	$P_2$ .	$\mu \times 10^{18}$ .
0.01124	0.8868	2.2387	54.26	0

(a) Present author.

(b) Recalculated from the data by H. Wild (1944).

TABLE II  
Table of moments  
 $\mu \times 10^{-18}$ .

Substance.		Substance.	$\mu \times 10^{-18}$ .
(1) 	1.10	(7) 	2.14
(2) 	0.0	(8) 	1.91
(3) 	1.66	(9) 	2.12
(4) 	1.55	(10) 	1.68
(5) 	1.90	(11) 	2.11
(6) 	1.18	(12) 	2.4
(13) 			2.5

No. 1, 2—Present author.

No. 3—13—Recalculated from the data by H. Wild (1944).

## DISCUSSION

The results are summarised in Table II. The applicability of the new equation to the various solutions is fully borne out by the constancy of the results. The small variations of the moment e.g., from 1.00 to 1.05 in the case of pure molten liquid and also 1.03 to 1.11 in the case of benzene solution are within the limits of experimental errors, as also the moments obtained from dioxane and carbon tetrachloride viz., 1.12 and 1.19D. Taking the new values of bond moments, C—H 0.4, C—Cl (aliph.) 1.69, C—Cl (arom.) 1.5, the average free rotation value along the various bonds comes to be the same as the observed moment for *p*:*p'*-DDT.

The dehydrochlorinated compound  $(C_6H_4Cl)_2C=CCl_2$  is a symmetrical molecule and should not possess any moment, which is confirmed by the present experimental work.

In the case of dichlorodiphenyltrichloroethane, the moment of *p*:*p'* compound is the least (1.1D) and that of the *o*:*p'* is the greatest (1.9D), *m*:*p'* being intermediate (1.55).

The moments of (Table of moments, Table II) *p*:*p'*-ditolyl-(Muller, *loc. cit.*), 3:3':4:4'-tetramethyl and 2:2':1:4'-tetramethyl-diphenyltrichloroethane are the same (viz., 2.1D) and which correspond to the free rotation along the HC—CCl<sub>3</sub>. In the case of 2:2':5:5'-tetramethyldiphenyltrichloroethane (West and Campbell, *loc. cit.*) the methyl groups being at *p*:*p'* position, the small moment due to CH<sub>3</sub> groups is cancelled and the resultant moment (1.66D) is the same as that of diphenyltrichloroethane (Muller, *loc. cit.*).

*Toxicity and the Dipole Moment of DDT and related Compounds*

It has been observed that in this series of compounds only DDT has highest insecticidal property. The mortality coefficients of these compounds have been calculated by applying the law of unimolecular reaction,

$$K = \frac{2.3}{t} \log \frac{100}{100 - x}$$

where *x* is the % of insects killed in time *t* (The full paper will be published elsewhere). The values are given in the following table

TABLE III

Compound	Mortality coefficient <i>K</i>	<i>x</i> × 10 <sup>18</sup>	Log <i>K</i> .
<i>p</i> : <i>p'</i> -DDT	14.6	1.10	1.16
<i>m</i> : <i>p'</i> -DDT	2.6	1.55	0.42
<i>o</i> : <i>p'</i> -DDT	1.3	1.90	0.21

It is interesting to point out the linear relationship between the logarithm of mortality coefficient and the dipole moment, as the moment increases, the mortality coefficient decreases, the compound DDT with lowest dipole moment (1.1D) being the most toxic insecticide (*K* = 14.6).

Thanks of the author are due to Dr. S. K. K. Jatkari for guidance and to the Council of Scientific and Industrial Research for the financial help during this investigation.

## CONDENSATION OF ALDEHYDES WITH MALONIC ACID. PART XXVI. CONDENSATION OF DIHYDROCINNAMALDEHYDE

RAGHUVIR RAJ BHANDARI AND KANTILAL C. PANDYA

Dihydrocinnamaldehyde has been condensed with malonic acid under different conditions. In the presence of pyridine or piperidine,  $\gamma$ -benzylcrotonic acid is obtained, the yield of which under certain conditions goes up to about 55%. In the absence of any condensing agent as well as under other conditions, the dibasic dihydrocinnamylidene-malonic acid is obtained, the yield of which in a pure form does not exceed 25%. It has not been described before in literature.

Dihydrocinnamic aldehyde has not been condensed with Perkin's reagents, or with malonic acid outside this laboratory. Kunin and Pandya (*J. Indian Chem. Soc.*, 1934, **11**, 825) condensed it with malonic acid in the presence of pyridine (0.15 mol.) by heating it on a water-bath for 4 hours and reported a yield of 29% of  $\gamma$ -benzylcrotonic acid.

This aldehyde is of particular interest as it may be looked upon as being more aliphatic than its close relative, cinnamaldehyde. For, though both have a common phenyl group, that group is connected in cinnamaldehyde by means of a conjugated double bond system, even beyond the benzene ring, with the aldehyde group; but in dihydrocinnamaldehyde this last double bond outside the ring disappears and the reactivity of the aldehyde group is now found to be considerably impaired. Thus cinnamaldehyde, like most of the other benzaldehyde-derived aromatic aldehydes, condenses easily with malonic acid, giving a 96% yield of cinnamylidene-malonic acid and 61% yield of the corresponding monobasic cinnamylidene-acetic acid (Gupta and Pandya, *ibid.*, 1947, **24**, 445). Dihydrocinnamaldehyde, on the other hand, has been so slow to combine that it gives about 25% yield of the dibasic acid and not more than 55% yield of the monobasic acid.

Of the many condensation experiments made in this laboratory, only a few typical ones are described in this paper. The monobasic acid came out in the presence of either piperidine or pyridine. The dibasic acid was obtained under a variety of conditions, such as in ether, in glacial acetic acid, in the absence of any solvent or of any condensing agent, or with fairly long heating on the water-bath. It was a yellow substance melting at 198-99°.

The dibasic acid,  $C_6H_5 \cdot CH_2CH_2CH : C(COOH)_2$ , is claimed to have been prepared by Thiele and Meisenheimer (*Annalen*, 1899, **306**, 260; cf. Beilstein, Band IX, 1926, p. 905) and is reported as  $\delta$ -phenyl- $\alpha$ -butylene- $\alpha\alpha$ -dicarboxylic acid. They heated the isomeric  $\delta$ -phenyl- $\beta$ -butylene- $\alpha\alpha$ -dicarboxylic acid (m. p. 106-108°, decomp.) on a water-bath with caustic soda for a long time, but their product melted at a low temperature, 115-16°. Ruber (*Ber.*, 1904, **37**, 3123) seems to have prepared the same acid by keeping the isomeric acid with fuming sulphuric acid at room temperature for one month and his product had a slightly higher melting point, 124°. Both the workers depended on a shift of the double bond under rather drastic conditions, but there is no evidence

that the reaction had completed itself or that the product was not a mixture of the two isomers. On the other hand, the purity of the product in the condensation in the presence of pyridine, particularly in aliphatic aldehydes, is evident (Harding and Weizmann, *J. Chem. Soc.*, 1910, **97**, 299; vide also Beilstein, 1926, Band IX, p. 905). It is equally true that, as Boxer and Linstead (*J. Chem. Soc.*, 1877, **31**, 738) have pointed out, the condensation of the aliphatic aldehydes gives on the whole a much smaller yield.

### EXPERIMENTAL

*γ-Benzylcrotonic Acid*.—Dihydrocinnamaldehyde (1.34 g.), malonic acid (1.034 g) and pyridine (6.13 c.c.) (1:1:0.15 mol.) were heated on a water-bath for 11 hours. A semi-solid mass that appeared next morning was taken out as usual; a milky white precipitate was obtained, melting at 101°, and, after recrystallisation (alcohol), melting finally at 103.5–104°. It agrees with the melting point 104° given in literature (Fittig and Hoffmann, *Annalen*, 1894, **283**, 304; vide, Beilstein, 1926, Band IX, p. 621). (Found: Equiv., 177.5; benzylcrotonic acid,  $C_{11}H_{12}O_2$  requires equiv., 176). The yield of the pure acid was 13.8%.

In 1:1:1 mol. proportions, the same materials gave 18.5% yield, and heating at 120°–130° for 7 to 8 hours gave 21% yield. With piperidine (3 drops) instead of pyridine, and 8 hours' heating at 110°–120°, the yield was a little less, 18.8%.

Heating at 180° for about 2 hours gave the mono-acid in the highest yield, namely 55%.

*Dihydrocinnamylidene-malonic Acid*.—The aldehyde and the malonic acid were heated alone on a water-bath for 5 hours; the mass fused in 2 hours and then became pink, solidifying gradually again after 4 hours. After the usual treatment a yellowish product was obtained, m. p. 192.5–193.5° (effervescence). After several recrystallisations the final melting point was 198–99° (effervescence). (Found: Equiv., 110.88; dihydrocinnamylidene-malonic acid,  $C_{12}H_{10}O_4$  requires equiv., 110; the mono-acid requires equiv., 176). The yield of the dibasic acid was 15.8%.

The acid is soluble in alcohol, chloroform, acetone and benzene, less in ether, still less in water and in glacial acetic acid. It decolorises Bayer's reagent and bromine water.

Heating for 7 hours, instead of 5, raised the yield to 20%, while a higher temperature, 110°–115° (6 hours) gave 22% yield. Still higher temperatures or longer heatings decomposed the dibasic acid to the monobasic and gave mixtures of the two acids; thus 13 hours' heating on a water-bath gave a product melting at 179°. Ten hours' heating on a water-bath gave, however, pure dibasic acid in 25% yield. Heating with glacial acetic acid (Stuart, *J. Chem. Soc.*, 1888, **53**, 142) or with ether gave very poor yields of the dibasic acid.

The thanks of the authors are due to Mr. Brahma Swarup Gupta who made the first experiments in this laboratory much earlier.

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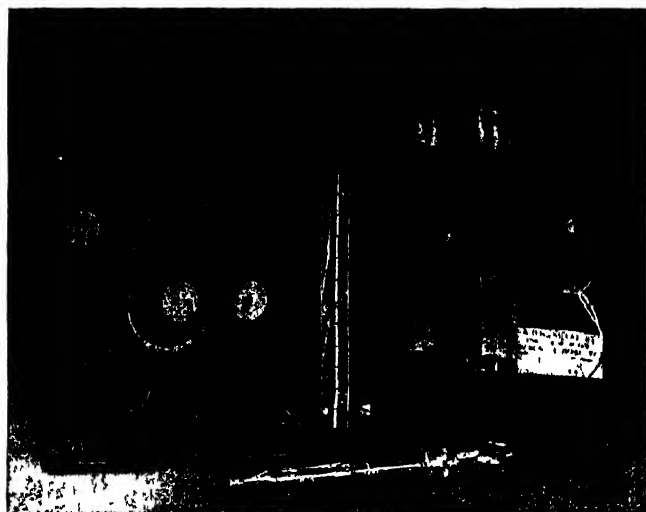
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## STUDIES ON THE TURBIDITY OF COLLOIDAL SUSPENSIONS OF LAYER LATTICE MINERALS

BY S. K. SINHA

The changes in turbidity of aqueous suspensions of bentonite, kaolinite and muscovite mica have been followed with progressive dilution, and the relative intensities of scattered light, which is the reciprocal of turbidity, are plotted against concentration. All the curves show well defined maxima and the concentrations of the colloidal salts corresponding to the maxima depend on the nature of the exchangeable cations. The minerals studied show characteristic differences as regards the above two.

According to Ostwald ("Licht und Farbe in Kolloiden", Dresden, 1924) turbidity of a suspension may be defined as the reciprocal of the intensity of light scattered by the particles in suspension. The theory of the scattering of light has been developed from various points of view. Rayleigh (*Phil. Mag.*, 1899, **47**, 375) studied the diffraction of extremely small particles as a function of size.

The case of spherical metallic particles of large diameters was developed by Mie (*Ann. Physik*, 1908, **25**, 377) and also by Debye (*ibid.*, 1909, **30**, 57). Gans (*ibid.*, 1912, **37**, 88 ; 1915, **47**, 270) investigated the influence of deviations from spherical shape. Rayleigh's theory is shown to be a special case of Mie's when the size of the particle is less than the wave-length of the incident light. As the particles become coarser in size, the intensity of scattered light increases till the size reaches the order of the wave-length of the light, after which the intensity decreases, preceded by a maximum. Mie's theory has been experimentally verified by a number of investigators (Bechold and Heber, *Kolloid Z.*, 1922, **31**, 8 ; Gribnaum, *ibid.*, 1936, **77**, 289 ; 1938, **82**, 15 ; Casperson, *ibid.*, 1932, **60**, 151) using colloidal solutions.

In the experiments done for the verification of Mie's theory in the case of colloidal suspensions mostly hydrophobic sols were used. Colloidal particles of clay minerals have a layer lattice structure, and hence non-spherical in shape. Moreover, they are more or less hydrated and get dispersed in water, the extent of dispersion depending on the nature of the minerals as well as on the exchangeable cation saturating it. Thus, the well known high dispersity of alkali-saturated clays is taken advantage of in determining the clay content of soils. The amount of dispersion will naturally depend on the ratio of colloid to water, which is the usual dispersion medium. When therefore a colloidal clay is diluted with water, the original particles will no doubt be reduced in number, but they will produce by dispersion or disaggregation particles of smaller sizes, which will increase in number and become still finer as dilution proceeds, until a limiting size, if any, is reached. In view of these two non-exclusive effects it becomes interesting to follow the changes in turbidity of aqueous colloidal suspensions of these minerals with progressive dilution.

### EXPERIMENTAL

The clay fractions obtained from the following samples of minerals were used for the present investigation.

1. Bentonite, containing the only clay mineral montmorillonite.
2. Muscovite mica.
3. Kaolinite.

The clay fractions from the powdered bentonite and kaolinite were obtained according to the International Soda method (Wright, "Soil Analysis", 1939). Sheets of mica were cut into very small pieces and then wet-ground in an electrically driven agate mortar and pestle. The clay fraction was afterwards separated by sedimentation. They were then converted into the hydrogen systems by continuous leaching with dilute hydrochloric acid, washed with distilled water and finally suspended in conductivity water. Portions of the hydrogen systems were converted into

the colloidal salts of Na, K, Ca and Ba (Mukherjee, *Indian Soil Sci. Bull.*, 1942, No. 4, p. 188) by adding to them the corresponding alkalis in amounts equivalent to the base exchange capacity of the clays as measured by the method of Parker (*J. Amer. Soc. Agron.*, 1929, **21**, 1030). The mixtures of the clay and alkalis were kept for about a month to attain equilibrium. The colloid contents of the suspensions were calculated in terms of the hydrogen systems. The relative turbidity of the suspensions as obtained directly from the drum-head reading of the Zeiss Trubungsmesser, is the reciprocal of the relative intensity of scattered light recorded in the diagrams below.

The colloidal salts taken from the stock solutions were diluted with known quantities of conductivity water in steam-cleaned Jena bottles and allowed to attain hydration equilibrium. The turbidities observed from day to day varied until after about a week constant values were obtained.

TABLE I

Conc. (g. per litre.)	Turbidity.	Reciprocal of turbidity (i.e. intensity).	Intensity for 1 g. per litre.	Intensity × conc.
Potassium bentonite sol.				
0.218	42.0	0.0240	0.110	—
0.254	38.0	0.0263	0.103	—
0.305	29.0	0.0345	0.113	—
0.380	25.0	0.0400	0.105	—
0.610	15.0	0.0666	0.109	—
1.220	10.0	0.1000	0.082	—
1.830	9.0	0.1110	0.0607	0.203
2.440	11.0	0.0900	0.037	0.219
8.050	13.0	0.0770	0.025	0.234
3.660	18.0	0.0555	0.015	0.201
4.270	21.0	0.0480	0.011	0.204
4.880	27.0	0.0370	0.0075	0.181
5.490	29.5	0.0340	0.0061	0.186
Potassium kaolinite sol.				
0.2127	14.0	0.0714	0.3355	—
0.2360	13.0	0.0769	0.3258	—
0.266	12.5	0.0800	0.3007	—
0.304	12.0	0.0833	0.2740	—
0.3545	11.5	0.0870	0.2454	—
0.4254	11.0	0.0909	0.2136	0.039
0.5317	13.5	0.0740	0.1390	0.039
0.709	15.5	0.0645	0.0909	0.045
0.85	19.5	0.0512	0.0602	0.043
1.7	48.0	0.0208	0.0122	0.036
2.55	82.0	0.0122	0.0047	0.031
3.40	166.5	0.0060	—	—
Potassium mica sol.				
0.027	83.0	0.012	0.444	—
0.055	47.0	0.021	0.381	—
0.110	23.5	0.0425	0.386	—
0.221	13.5	0.074	0.334	—
0.442	10.5	0.095	0.214	0.042
0.885	15.0	0.066	0.074	0.058
1.77	25.0	0.040	0.022	0.071
3.54	52.0	0.019	0.005	0.071

*N.B.*—Similar results have been observed in other bentonites, micas and kaolinites but are omitted for want of space.

TABLE II

System.	Colloid content corresponding to maximum intensity in g. per litre.	Value of maximum intensity per g. of colloid.
Sodium bentonite	3.05	0.0280
Hydrogen bentonite	1.008	0.135
Potassium bentonite	1.830	0.0607
Barium bentonite	1.220	0.091
Potassium kaolinite	0.4254	0.2136
Barium kaolinite	0.3545	0.2560
Calcium kaolinite	0.3545	0.2967
Sodium mica	0.442	0.25
Potassium mica	0.442	0.214

## DISCUSSION

The variations of the relative intensity of scattered light of the different colloidal salts with concentration are graphically shown in Figs. 1-3. The following points of interest emerge from them.

FIG. 1

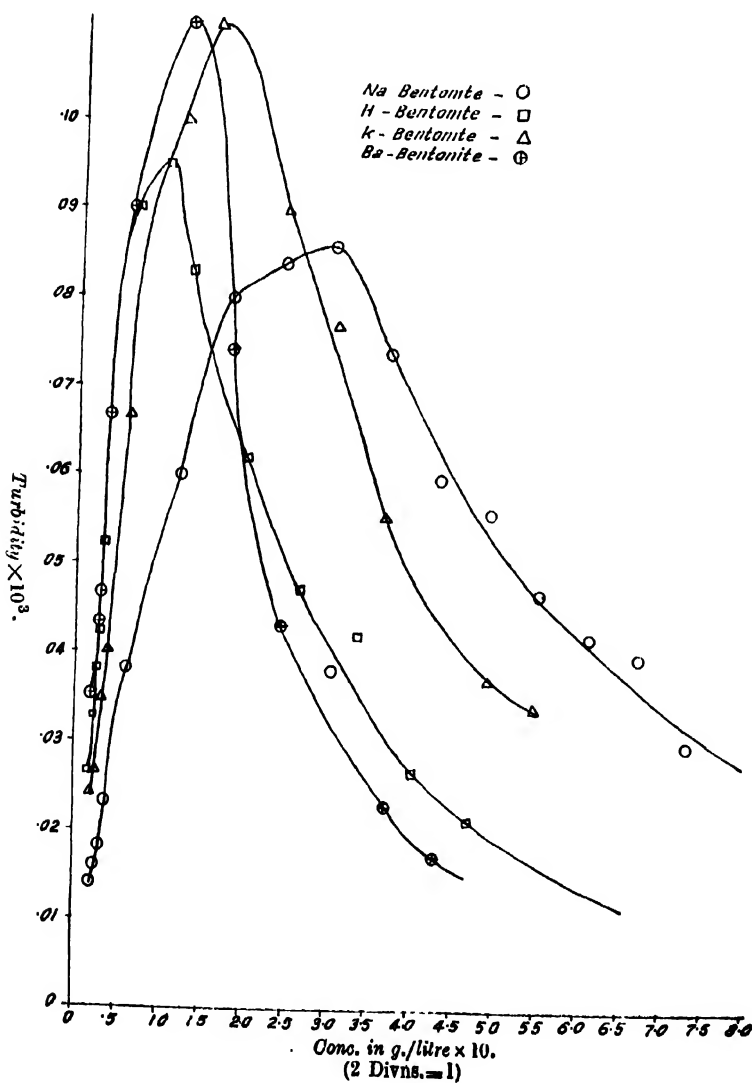
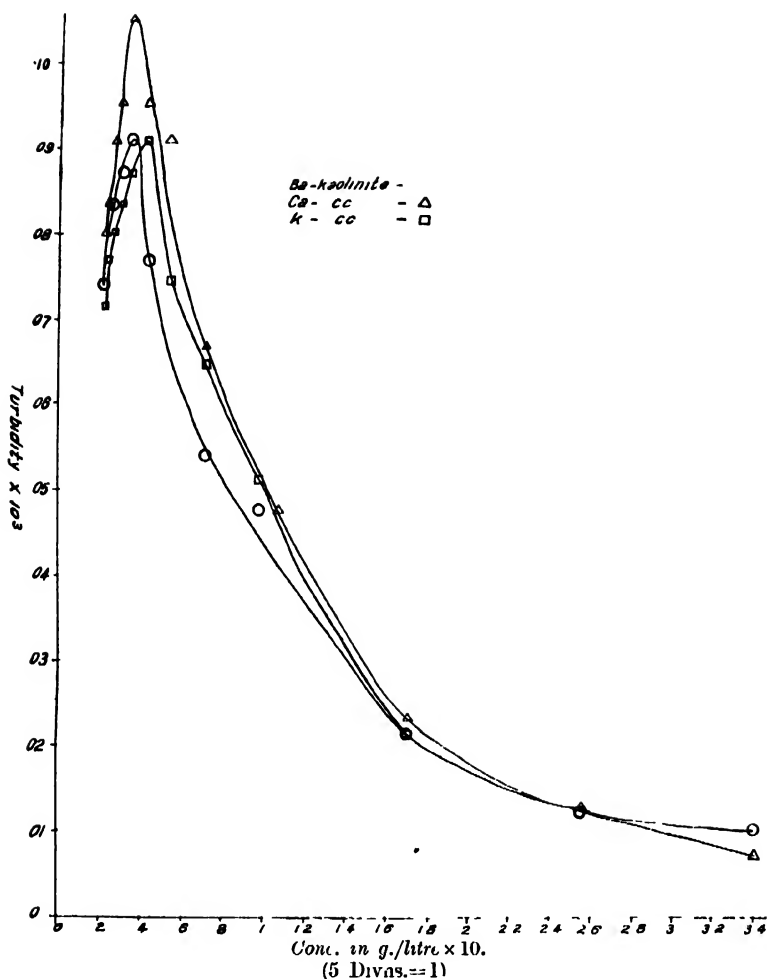


FIG. 2



All the curves show well defined maxima ; the concentrations of the colloidal salts corresponding to the maxima depend on the nature of the exchangeable cations ; and the minerals studied show characteristic differences as regards the above two.

The sizes of the colloidal particles vary within a wide range. The size distribution is not known, but the largest particles are of the order of  $10^{-4}$  cm. and the smaller, of the order of  $10^{-6}$  cm. Moreover, the particles are non-spherical in shape. Rayleigh's theory is therefore applicable to these systems only in a restricted sense.

The curves showing the maxima are similar to the intensity of scattered light size variations as demanded by the theory. A progressive change in particle size with dilution is thus indicated. This appears to fit in with the following picture of the state of affairs. In the most concentrated sols studied the minerals happen to be considerably aggregated, the particle size of the aggregates being large enough to obey Mie's theory. Dilution decreases the number of aggregates, as well as breaks them into those of smaller sizes which are still large enough to obey Mie's theory. Towards the initial stages, i.e. the low dilution range, the latter effect appears to be prominent. The right hand part of the curve, which is hyperbolic in nature, depicts this condition. The

constancy of the product of the relative intensity and colloid concentration (cf. Table I, column 5) corroborates the same. At higher dilutions disaggregation takes place to a greater extent and the effect of particle size becomes more and more predominant. The particles having the critical sizes necessary for Rayleigh's law to hold good gradually increase in number so that the intensity of scattered light begins under the circumstances to decrease. The two opposing effects give rise to a maximum after which disaggregation no longer takes place, *i.e.*, at this concentration of the colloid corresponding to the maximum it disperses into the ultimate size. Further dilution therefore causes a decrease in the number of these smallest particles. Since the effect of particle size is more predominant, the decrease in the intensity ( $I$ ) of scattered light after the maximum is very sharp. The fact that the value of  $I$  in the range of high dilutions after the maximum is almost constant (vide Table I, column 4), when expressed per unit weight of the colloid, suggests that dilution in this region causes only a proportionate decrease in the total number of scattering centres, *i.e.*, particles. This can only happen if disaggregation is complete at or about the maximum.

FIG. 3

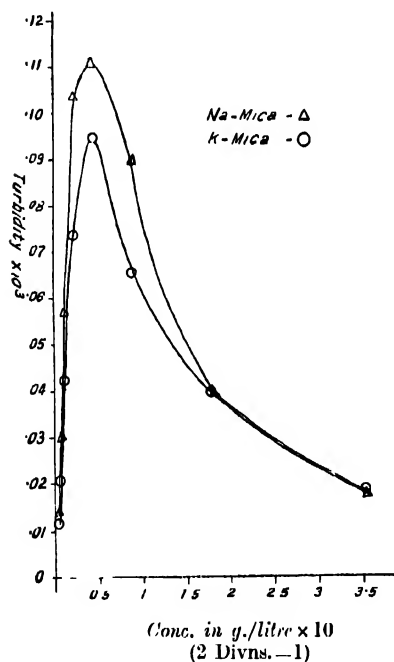
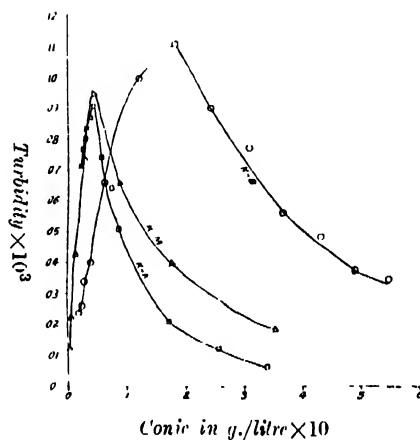


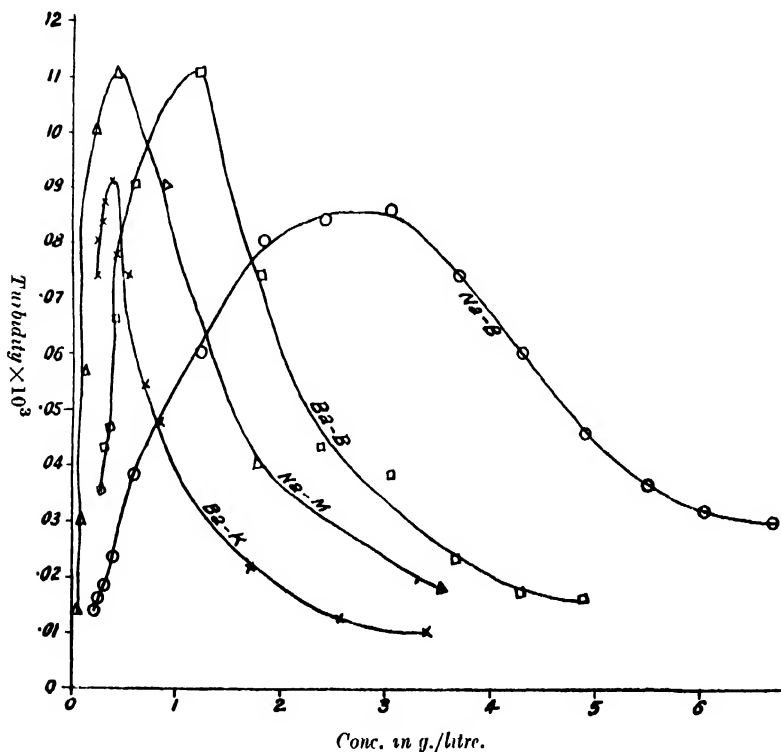
FIG. 4



It will be seen from Figs. 4 and 5, in which the colloids saturated with the same kind of cations have been compared, that the maximum values of  $I$  *i.e.*, the minimum turbidities occur at a higher concentrations of the montmorillonite than either the micas or kaolinities. This shows that the breaking up of the aggregates is complete at a higher concentration of the former than the latter. The mica and the kaolinite seem to show the maxima almost at the same concentration. This is expected if one takes into consideration the crystalline structures of these minerals. Montmorillonite is known to have a very open structure and to swell markedly in water. It is therefore highly unstable in its interaction with water. Mica and kaolinite have, on the other hand, compact structures and interact slowly with water so that disaggregation goes on up to very high dilutions.

The concentrations at which the minimum values of turbidity occur, as well as values of the latter, depend markedly on the nature of the saturating cation. In this connection the figures given in Table II are illustrative. The colloid content corresponding to almost the same order of the turbidity are much greater in the case of montmorillonites than in the micas and kaolinites (*vide supra*). The values of the maximum intensity expressed on the basis of 1 g. of the colloidal salts (column 3, Table II), when considered for a particular mineral, show a definite lyotropic effect of the saturating cations. For instance, the orders are:  $H > Ba > K > Na$  in montmorillonites;  $Ca > Ba > K$  in kaolinites; and  $Na > K$  in micas. K is a constituent of the mica lattice and causes a greater dispersion and a higher turbidity of K-mica compared to Na-mica suspensions.

FIG. 5



A comparison of the curves in Figs. 4 and 5 further shows that at the same concentration of the colloids, montmorillonites have much higher values of turbidity than the micas and the kaolinites. This once again points to the much more compact structure of the micas and kaolinites and the highly dispersed nature of the montmorillonites.

The author's thanks are due to Dr. S. K. Mukherjee of the University College of Science and Technology for suggesting the problem and giving laboratory facilities and to Dr. N. K. Sen, Head of the Department of Chemistry, Presidency College, for his kind interest.

## LOSS OF NITROGEN IN BACTERIAL NITRIFICATION

BY N. R. DHAR AND M. C. PANT

Contrary to the generally accepted idea that no marked loss of nitrogen takes place during bacterial nitrification of nitrogenous compounds, it has been observed that approximately half of the total nitrogen is lost in the nitrification of hippuric acid, oil-cake, uric acid, creatine and fibrin. With ammonium phosphate, sulphate, persulphate and urea the loss of nitrogen is more than half.

This loss has been explained from the view-point that during the process of nitrification, ammonium nitrite is produced as an intermediate product, which decomposes into water and nitrogen. The loss may also partially be due to the decomposition of nitrous acid, especially when the  $pH$  is less than 7.

The presence of carbonaceous substances retard the velocity of oxidation of ammonia to nitrate by acting as negative catalysts.

In previous publications (*J. Indian Chem. Soc.*, 1935, **12**, 67, 75 ; 1936, **13**, 555 ; 1938, **15**, 583) it has been shown that marked losses of nitrogen take place during the nitrification of organic and inorganic manures in soil cultures. Also the experiments at Rothamsted fields reveal that when 100 lbs. of nitrogen per acre are added, approximately 65% are lost without benefit to the soil or the crop.

On the other hand, the position regarding the bacterial nitrification in liquid cultures has been stated by Russell ("Soil Conditions and Plant Growth", 1932, p. 328) as follows :—

"The essential facts of nitrification are readily demonstrated by putting a small quantity of soil—0.2 to 0.5 gram into 50 c.c. of a dilute solution of ammonium sulphate containing nutrient inorganic salts and some calcium or magnesium carbonate but no other carbon compound. After three or four weeks at 25° the ammonia is all gone and its place taken up by nitrates. The conversion is almost quantitative, only an insignificant quantity of nitrogen being retained by the organisms."

In order to explain the difference in these observations we have undertaken a systematic research on the problem of nitrogen loss during bacterial nitrification of different substances, both organic and inorganic in liquid cultures.

### EXPERIMENTAL

The following medium was prepared for the growth of the nitrifying bacteria : Potassium phosphate ( $K_2HPO_4$ ), 1.0 g ; sodium chloride, 2.0 g., ferrous sulphate, 0.4 g., distilled water, 1000 c.c. and magnesium carbonate, excess (0.5 g. per 100 c.c.).

After shaking the medium, 50 c.c. of it were taken in 200 c.c. conical flasks which were then plugged with cotton wool and were sterilised in an autoclave at a pressure of 15 to 20 lbs. for half an hour. A 10% solution of ammonium sulphate was prepared and sterilised separately. From 1 c.c. to 10 c.c. of this solution was added to various flasks containing the sterilised media by a sterile pipette. For obtaining the nitrifying bacteria, one gram of fresh garden soil was inoculated into each experimental flask. The flasks were then incubated at 35° for a period of seven to eight weeks. A 10% solution of ammonium persulphate or ammonium phosphate was used in a similar manner as in the case of ammonium sulphate. For experiments with substances like hippuric acid, urea, oil-cake, fibrin etc., a known amount of the substance was weighed and placed in the flask containing the medium. The flasks were then sterilised along with these nitrogenous substances. The analysis was performed in the following manner.

The ammoniacal nitrogen was estimated colorimetrically by Nessler's reagent. Nitric nitrogen was reduced by Devarda's alloy to ammoniacal nitrogen and then estimated as above. For total nitrogen, the Kjeldahl method was used. The following results have been obtained.

TABLE I

Ammonium sulphate as the source of nitrogen.

Original N content Soln. Nitrogen.	Ammon. N left.	Nitric N formed.	Total N left.	N lost.	% Loss of nitrogen.
10.0 c.c. 0.2121 g.	0.1328 g.	0.0178 g.	0.1506 g.	0.0615 g.	38.9
7.0 0.1485	0.0776	0.0160	0.0936	0.0549	27.1
5.0 0.1061	0.0289	0.0152	0.0441	0.0620	58.4
2.0 0.0424	0.0031	0.0118	0.0149	0.0275	64.6
1.5 0.0318	0.0019	0.0080	0.0099	0.0219	68.5
1.3 0.0275	0.0008	0.0041	0.0049	0.0226	81.8
1.0 0.0210	0.0005	0.0034	0.0039	0.0171	82.0

TABLE II

Ammonium persulphate as the source of nitrogen.

Period of incubation : 30-7-47 to 20-9-47.

Original N content Soln. Nitrogen.	Ammon. N left.	Nitric N formed.	Total N left.	N lost.	% Loss of N.
10.0 c.c. 0.3158 g.	0.2428 g.	0.0310 g.	0.2738 g.	0.0420 g.	13.3
7.0 0.2211	0.1472	0.0220	0.1692	0.0519	23.1
5.0 0.1579	0.0888	0.0182	0.1070	0.0590	32.2
3.0 0.0947	0.0272	0.0142	0.0414	0.0533	56.3
1.0 0.0316	0.0000	0.0113	0.0113	0.0203	61.2

TABLE III

Ammonium phosphate as the source of nitrogen. Period of incubation : 20-12-47 to 27-2-48.

Original N content Soln. Nitrogen.	Ammon. N left.	Nitric N formed.	Total N left.	N. lost	% Loss of N.
7.0 c.c. 0.1485 g.	0.0718 g.	0.0180 g.	0.0894 g.	0.0591 g.	39.8
5.0 0.1061	0.0328	0.0072	0.0400	0.0661	62.3
2.0 0.0424	0.0069	0.0055	0.0124	0.0300	70.7

TABLE IV

Gelatine as the source of nitrogen. Period of incubation : 20-12-47 to 27-2-48.

Original N content Substance. Nitrogen.	Total N left.	Ammon. N formed.	Nitric N formed	N lost.	% Loss of N.
40.0 c.c. 0.0992 g.	0.0517 g.	0.0072 g.	0.0102 g.	0.0475 g.	47.8
20.0 0.0496	0.0204	0.0017	0.0041	0.0292	58.8
10.0 0.0248	0.0081	0.0008	0.0022	0.0167	67.3

TABLE V

Urea as the source of nitrogen. Period of incubation : 4-8-48 to 23-9-48.

Original N content Substance. Nitrogen.	Total N left.	Ammon. N formed.	Nitric N formed.	N lost.	% Loss of N.
0.4286 g. 0.2000 g.	0.1202 g.	0.0101 g.	0.0197 g.	0.0798 g.	39.9
0.2143 0.1000	0.0486	0.0063	0.0122	0.0312	51.2
0.1072 0.0500	0.0198	0.0024	0.0062	0.0302	60.4



TABLE VI

Huppuric acid as the source of nitrogen. Period of incubation, 29-7-48 to 17-9-48.

Original N content Substance. Nitrogen.	Total N. left.	Ammon. N formed.	Nitric N. formed.	N lost.	% Loss of N.
2.5572 g.      0.2000 g.	0.0112 g.	0.0125 g.	0.0125 g.	0.0798 g.	39.9
1.2786        0.1000	0.0500	0.0067	0.0073	0.0500	50.0
0.6394        0.0500	0.0210	0.0032	0.0041	0.0290	58.0

TABLE VII

Oil-cake as the source of nitrogen (Nitrogen content of oil-cake used=5.0%)  
Period of incubation, 4-8-48 to 23-9-48.

Original N content Substance. Nitrogen.	Total N left.	Ammon. N formed.	Nitric N formed.	N lost.	% Loss of N.
4.0 g.        0.2000 g.	0.1258 g.	0.0064 g.	0.0053 g.	0.0732 g.	36.6
2.0        0.1000	0.0513	0.0041	0.0037	0.0487	48.7
1.0        0.0500	0.0213	0.0014	0.0020	0.0287	57.4

TABLE VIII

Uric acid as the source of nitrogen. Period of incubation : 23-7-48 to 10-9-48.

Original N content Substance. Nitrogen.	Total N left.	Ammon. N formed.	Nitric N formed.	N lost.	% Loss of N.
0.60 g.        0.2000 g.	0.1224 g.	0.0062 g.	0.0025 g.	0.0776 g.	38.8
0.30        0.1000	0.0514	0.0051	0.0021	0.0486	48.6
0.15        0.0500	0.0218	0.0040	0.0015	0.0282	56.4

TABLE IX

Fibrin as the source of nitrogen (Nitrogen content of fibrin used—14.7%)  
Period of incubation : 29-7-48 to 17-9-48.

Original N content Substance. Nitrogen.	Total N left.	Ammon. N formed.	Nitric N formed.	N lost.	% Loss of N.
1.40 g.        0.2058 g.	0.1327 g.	0.0095 g.	0.0351 g.	0.0731 g.	35.5
0.70        0.1029	0.0601	0.0048	0.0021	0.0428	41.7
0.35        0.0515	0.0256	0.0019	0.0013	0.0259	50.3

TABLE X

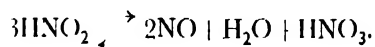
Creatine as the source of nitrogen. Period of incubation : 23-7-48 to 10-9-48.

Original N content Substance. Nitrogen.	Total N left.	Ammon. N formed.	Nitric N formed.	N lost.	% Loss of N.
0.6238 g.      0.2000 g.	0.1260 g.	0.0081 g.	0.0038 g.	0.0740 g.	37.0
0.3119        0.1000	0.0538	0.0043	0.0022	0.0462	46.2
0.1560        0.0500	0.0240	0.0024	0.0013	0.0260	52.0

## DISCUSSION

The foregoing experimental results show that even during the process of nitrification of ammonium salts or other nitrogenous compounds, under conditions quite favourable for the growth of bacteria, there is a considerable loss of nitrogen. The mechanism of reactions involved in liquid cultures appears to be the same as in soil cultures when nitrogenous manures are added to the soil under the field or laboratory conditions.

The loss of nitrogen during the nitrification has been explained by us on the view-point that during nitrification, the ammonium ions and nitrite ions, present simultaneously, combine to give ammonium nitrite, which being an unstable compound decomposes into water and nitrogen. In case of soils having a *pH* greater than 7, some nitrogen may be lost as ammonia gas; but under ordinary conditions, on adding nitrogenous manures, the *pH* goes to the acid side and the loss may be partially due to the decomposition of nitrous acid according to the equation:



Our results further show that the loss of nitrogen and the nitrification are much more pronounced with ammonium salts than with other nitrogenous substances. The greater loss in case of ammonium salts is due to the possibility of larger amounts of ammonium nitrite being formed on account of the easy nitrification of the ammonium ions present. In the case of substances like oil-cake, creatine, fibrin and uric acid, the loss is less, as is clear from the following table.

TABLE XI

No.	Substances	Nitric N formed	% Loss of N.	No.	Substances	Nitric N formed	% Loss of N.
1.	Ammon. phosphate	7.2 mg	62.3	6.	Oil cake	3.7 mg	48.7
2.	Ammon. sulphate	15.2	58.4	7.	Uric acid	2.1	48.6
3.	Ammon. persulphate	14.2	56.3	8.	Creatine	2.2	46.2
4.	Urea	12.2	51.2	9.	Fibrin	2.1	41.7
5.	Hippuric acid	7.3	50.0				

In substances other than ammonium salts, the nitrogen is present in a complex condition and hence is slowly nitrified. Moreover, they contain carbon along with nitrogen and the carbonaceous substances present or formed act as negative catalysts and retard the oxidation of the nitrogenous compounds and the consequent loss of nitrogen.

## ESSENTIAL OIL FROM THE LEAVES OF BÊL (*AEGLA MARMELLOS*)

BY K. K. BASIAS AND S. S. DESHAPANDE

Essential oil is extracted from the leaves of *Aegle marmelos*. Its chief component is found to be  $\alpha$ -*d*-phellandrene which forms about 56% of the oil.

The tree of *Aegle marmelos*, popularly known in vernacular as Bêl and in Sanskrit as 'Bilwa' is indigenous to India and belongs to the family of Rutaceae.

The earliest reference to the essential oil extracted from the leaves of the plant is found in Gildmeister and Hoffmann's treatise (The Ethereal Oils, Vol. III, p. 648). The relevant part of the reference is quoted below :—

"According to a communication by Ritsemma (J. nat. dep. landb. in NedIndie Batavia, 1908, p.52) the leaves yielded upon distillation about 0.6% of an oil with a light yellow colour,  $d_{25}^{20}$ , 0.856;  $n_D^{20}$ , 10.71. Distillation resulted in the following fractions :

I (up to 100°), 5g, II (100° to 130°), 5.1g., III (130° to 160°), 1g. Residue, 1.5 g.

Fraction II contained limonene which was characterised by its boiling point (175°) and its tetrabromide (m.p. 104°). Aldehydes could not be detected. On prolonged standing the oil becomes viscid."

Dikshit and Dutta (J. Indian Chem. Soc., 1930, 7, 759) extracted dried leaves of the plant with various solvents and obtained tannin, reducing sugars, etc. They make no reference about the occurrence of the terpenes or any odoriferous component which obviously must have been lost during the drying of leaves. With a view therefore to ascertaining the chemical composition of the oil of Indian source we have extracted the oil from fresh leaves of Bêl the composition of which (Table I) differs widely from that of the oil referred to by Gildmeister and Hoffmann (*loc. cit.*).

The leaves on steam-distillation gave an oil in 0.6% yield. It was noticed that the yield of the oil from young leaves was somewhat greater than from the mature leaves. The oil gave the following properties.

TABLE I

I. $d_{20}^{20}$	..	..	..	0.8476	IV. Acid value	..	..	..	2.9
II. $n_D^{31}$	..	..	..	1.4750	V. Sapon. value	..	..	..	16.1
III. $n_D^{20}$	..	..	..	52.1	VI. Citral content of oil*	..	..	..	3.76%

\* By the method of thiosemicarbazide of Radcliffe and Swann (*Prof. & Ess. Oil Rev.*, 1928, 19, 47)

On careful fractionation of the oil under reduced pressure three fractions were collected whose properties and % yield are shown in Table II. Fraction I constituting about 56% of the oil is presumed to be a single substance, as on repeated distillations under atmospheric pressure it boiled within a narrow range of 173° to 175°. Quantitative analysis, however, showed that this fraction consisted mostly of a terpene mixed with a small proportion of an oxygen containing compound. The terpene formed a nitrosite (m.p. 105°). From the boiling point of the terpene and the melting point of its nitrosite, as also from other properties shown in Table III, the terpene has been identified as  $\alpha$ -*d*-phellandrene.

The oxygen containing compound intimately mixed with the terpene gave reactions of cineol. Thus fraction I, when shaken with syrupy phosphoric acid, gave a semisolid mass on cooling which is a characteristic of cineol. Further, when this fraction was warmed with a little iodol (tetra-iodopyrrole,  $C_4I_4NH$ ) the additive compound of cineol and iodol separated as a yellowish green crystalline mass (cf. Bertram and Walbaum, *Arch. Pharm.*, 1897, **235**, 178). The quantity, however, was insufficient for further purification by crystallisation. These products of cineol were compared by us with the corresponding products which we prepared from pure cineol isolated from authentic specimen of eucalyptus oil.

The separation of  $\alpha$ -*d*-phellandrene from cineol in fraction I was effected by washing the fraction with 50% aqueous resorcinol in which the cineol dissolved (in the form of its addition product with resorcinol) (*Sch. Ber.*, 1907, **5**, 32). The phellandrene which remained undissolved gave on purification and analysis results agreeing with the composition  $C_{10}H_{16}$ . The cineol separated from resorcinol solution on addition of alkali and boiled at  $176^\circ$ .

The nitrosite of phellandrene prepared by us melted at  $105^\circ$ , but on recrystallisation its melting point rose to  $113^\circ$ . Read and Storey (*J. Chem. Soc.*, 1930, 2770) prepared nitrosite of  $\alpha$ -*d*-phellandrene which they obtained from piperitol by dehydration. The authors mention that the melting point of their nitrosite rose after crystallisation from  $105^\circ$  to  $110^\circ$  and finally to  $115^\circ$ .

We have noted like the previous observers that the optical rotation of the nitrosite of  $\alpha$ -*d*-phellandrene is opposite in direction to the rotation of the phellandrene itself. Thus  $\alpha$ -*d*-phellandrene forms a *laevo*-rotatory nitrosite (Wallach and Beschke, *Annalen*, 1904, **336**, 40), while  $\alpha$ -*l*-phellandrene forms a *dextro*-rotatory nitrosite (Read, *J. Chem. Soc.*, 1936, 1597). The specific rotation of the nitrosite of  $\alpha$ -*d*-phellandrene prepared by us was  $-47^\circ$  and it does not agree with the value given by Wallach, which is  $-138^\circ$ . Although we cannot explain the discrepancy at this stage, it must be pointed out that the phellandrenes as well as their nitrosites are very unstable. Different rotations have been recorded for phellandrenes obtained from different sources (Table III). The nitrosites of phellandrenes in solution exhibit mutarotation. Thus Read (*loc. cit.*) records that the rotation of  $\alpha$ -nitrosite of  $\alpha$ -*l*-phellandrene changes from  $+148^\circ$  to  $+130^\circ$  in 48 minutes and to  $-45.8^\circ$  in 115 hours. We observed that the rotation of the  $\alpha$ -nitrosite of  $\alpha$ -*d*-phellandrene prepared by us changed from  $-47^\circ$  to  $+42.6^\circ$  in 3 days.

Fraction II boiling between  $104^\circ$  and  $130^\circ$  130 mm. was redistilled at atmospheric pressure when most of it passed between  $205^\circ$  and  $208^\circ$ . It reduced Fehling's solution and showed general reactions of an aldehyde. The bisulphite compound of the aldehyde was prepared by the method of Tiemann (*Ber.*, 1898, **31**, 3307) and the semicarbazone, prepared directly from the bisulphite compound (Tiemann, *loc. cit.*), melted at  $84^\circ$ . From its boiling point and the melting point of its semicarbazone the aldehyde was identified as citronellal. Fraction II and the two derivatives (the bisulphite and the semicarbazone) were compared by us with the pure citronellal (prepared from Java citronella oil) and its two derivatives.

Fraction III began to distil above  $210^\circ$  at atmospheric pressure, but it soon became thick due to polymerisation. This also gave reactions of an aldehyde. Its bisulphite compound was prepared by Tiemann's method and directly from the latter the semicarbazone was prepared in presence of free acetic acid (distinction from the method for preparing citronellal semicarbazone). On crystallisation the semicarbazone melted at  $163^\circ$ . From the boiling range of the aldehyde, the formation of its semicarbazone in presence of free acetic acid, and the melting point of the semicarbazone, the aldehyde was identified as citral. The aldehyde and its derivatives were compared by us with pure citral (obtained by us from pure lemon grass oil from Holland) and its derivatives.

## EXPERIMENTAL

*Isolation of the Essential Oil.* The essential oil was obtained by steam-distillation of the leaves from a copper still fitted with a spiral copper condenser. The oil separated from the aqueous distillate as a light yellow layer floating over water. It was carefully separated from water which was returned to the still for next distillation. The oil, dried over calcium chloride, gave properties, shown in Table I.

*Fractionation of the Oil.* The oil (80 c.c.) was fractionally distilled at 130 mm. pressure. Three fractions were collected; the boiling ranges, percentage yields and properties of the fractions are shown in Table II.

TABLE II

No.	B. p. (130 mm.)	Vol.	Yield.	B. p. at atmospheric pressure.	Properties, M.p. of their deri- vatives.
I	80-104°	15 c.c.	56%	173-174	Nitrosite, 105°
II	104-130	17	21	205-208	Semicarbazone, 84°
III	130-160°	7	9	Above 210	Semicarbazone, 164°

*Isolation of Pure  $\alpha$ -d-Phellandrene from Fraction I.*—This fraction was distilled at atmospheric pressure when 40 c.c. were collected between 173 and 174°. The distillate was shaken with 50% aqueous resorcinol which dissolved cineol. The phellandrene remaining undissolved was repeatedly washed with water till free from resorcinol; it was dried and distilled from a flask with a fractionating column. The portion boiling at 174° was analysed. (Found: C, 88.0; H, 11.7.  $C_{10}H_{16}$  requires C, 88.2; H, 11.8 per cent).

*Isolation of Cineol.*—From the aqueous resorcinol solution the cineol was liberated by adding alkali, shaking vigorously and then extracting with ether. On drying and removing the solvent the residual liquid boiled at 176°.

*The Nitrosite.* To a solution of fraction I (10 c.c.) in petroleum ether (20 c.c.) was added an aqueous solution of sodium nitrite (10g. in 15 c.c.). After cooling well by freezing mixture glacial acetic acid (10 g.) was gradually added when the nitrosite began to separate as a white crystalline mass which was filtered, washed with water and finally with methyl alcohol. The crude dry nitrosite was purified by dissolving in chloroform and precipitating by the addition of methyl alcohol. It melted at 105°. By repeating the above process m.p. rose to 114°.

The nitrosite dissolves freely in chloroform and shows optical rotation,  $[\alpha]_D -47$  in that solvent. A comparison between the properties of the phellandrene obtained from the essential oil with those of this terpene described in literature is made in Table III.

TABLE III

No.	Properties.	Fraction I.	$\alpha$ -d-Phellandrene.
I.	B.p.	173° to 174°	172° (Pesci, <i>Ber.</i> , 1886, <b>19</b> , 874); 175° to 176° (obtained from ginger grass oil, Walbaum and Huthig, <i>J. prakt. Chem.</i> , 1905, <i>ii</i> , <b>71</b> , 460).
II.		1.477 (at 31°)	1.488 at 19°.
III.	$[\alpha]_D$	+49.1°	+44.1° (Walbaum & Huthig <i>loc. cit.</i> ); +17.61° (Pesci, <i>loc. cit.</i> ) 60.21° (Gildmeister and Stephens, <i>Arch. Pharm.</i> , 1897, <b>235</b> , 591.)
IV.	M.p. of nitrosite	105°	105° (Read & Storey <i>J. Chem. Soc.</i> , 1930, 2770.)

The  $\alpha$ -*d*-phellandrene was prepared by Read and Storey (*loc. cit.*) by dehydration of *d*-pi-peritol which was shown by Simonsen (*Indian Forest Records*, 1924, Part VIII, p. 10) to occur in the essential oil of a species of *Andropogon* growing in United Provinces.

*Sodium Bisulphite Compound and Semicarbazone of Citronellal.* -Fraction II, which when distilled at atmospheric pressure, boiled mostly between 205° and 208°. A cold saturated solution of sodium sulphite was added to 2 c.c. of this fraction kept cool by ice. On adding gradually glacial acetic acid (equivalent amount) and vigorous shaking crystals of the bisulphite compound began to separate. These were filtered off and freed from the adhering oil by pressing between filter papers and drying on a porous plate. The crystals were dissolved in excess of water and to the clear solution was added a strong solution of semicarbazide hydrochloride and sodium acetate. On cooling by freezing mixture and vigorous shaking the semicarbazone separated which was filtered off, dried and recrystallised from alcohol, m.p. 84° (citronellal semicarbazone, m.p. 86°.)

*Sodium Bisulphite Compound and Semicarbazone of Citral.* -The sodium bisulphite compound was prepared from fraction III in the manner described above. To the clear solution of this in water a solution of semicarbazide hydrochloride and sodium acetate together with free acetic acid were added. On cooling and shaking the mixture the citral semicarbazone separated. This on recrystallisation melted at 163° (semicarbazone from an authentic specimen of citral melted at 164°).

## STUDIES IN FRIES MIGRATION. PART IV. THE FRIES MIGRATION OF ACETOXYBENZOIC ACIDS

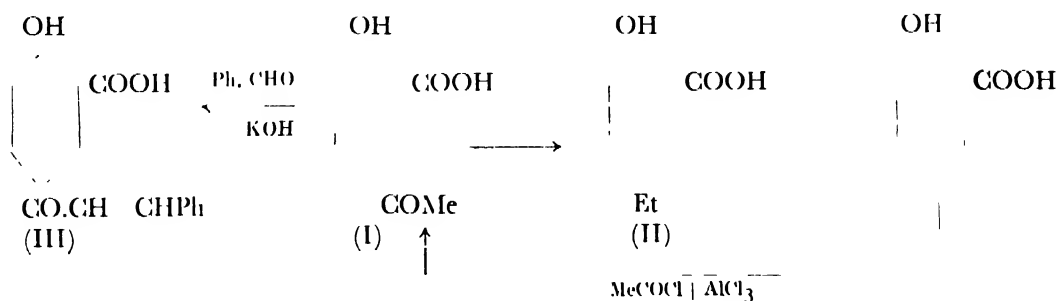
BY DHIRAJLAL N. SHAH AND NARSINH MOOLJIBHAI SHAH

The Fries migration of three isomeric acetoxybenzoic acids has been investigated. Aspirin gives 2-hydroxy-5-acetylbenzoic acid, the acetyl group migrating to the *para* position to the hydroxyl group; the *p*-acetoxybenzoic acid on migration gives 3-acetyl-4-hydroxybenzoic acid, the *ortho* migration taking place. Attempts to effect the migration of *m*-acetoxybenzoic acid failed, the *m*-COOH thus hindering the migration. The constitutions of the migration products obtained have been established.

In extension of the work on the Fries migration described in the previous parts of this series (Thakor and Shah, this *Journal*, 1946, **23**, 199, 234; Amin and Shah, *ibid.*, 1948, **25**, 377) the present investigation was undertaken to study the Fries migration of acetoxy derivatives of the three isomeric hydroxybenzoic acids.

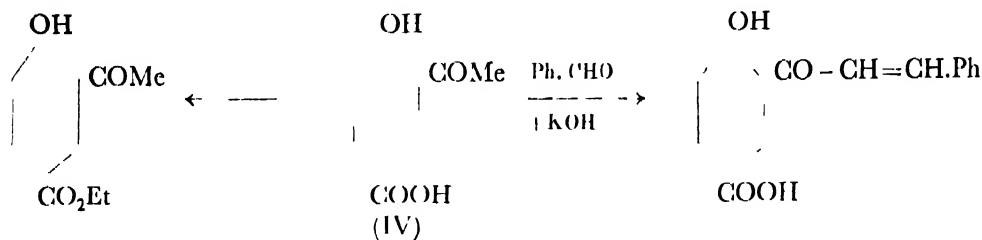
It has been shown earlier that the precise position taken up by the migration group is affected by the nature of the phenol. Rosenmund and Schnurr (*Annalen*, 1928, **460**, 56) studied the migration of differently substituted phenolic esters and found that nitro, acetyl and carboxylic groups in the phenol molecule inhibited the reaction. Recently, however, Brown (*J. Amer. Chem. Soc.*, 1946, **68**, 873) has successfully carried out the Fries migration of *o*-nitrophenyl acetate. Cox (*ibid.*, 1930, **52**, 352) studied the migration of some esters of methyl salicylate. His results show that the carbomethoxy group in the *ortho* position to the OH group does not hinder the migration. The perusal of literature showed that hardly any work has been done on the application of the Fries migration to the acetoxybenzoic acids. The migration of *o*-acetoxybenzoic acid (aspirin), *m*-, and *p*-acetoxybenzoic acids has been investigated under various conditions and the results are detailed below.

The migration of aspirin gives a product which has been assigned the constitution, 5-acetyl-2-hydroxybenzoic acid (I) on the following grounds: (i) It dissolves in sodium bicarbonate solution with effervescence, and in alkali with yellow colour; (ii) it gives wine-red colour with alcoholic ferric chloride; (iii) it gives an oxime and semicarbazone indicating the presence of ketonic group; (iv) on Clemmensen reduction it gives 5-ethyl-2-hydroxybenzoic acid (II) (Beilstein and Kuhlberg, *J. Russ. phys. chem. Gesell.*, **2**, 273; *Annalen*, 1870, **156**, 213); (v) it gives a chalkone (III) on condensation with benzaldehyde in presence of alkali, and finally (vi) it is identical with the product obtained by the Friedel-Crafts acetylation of salicylic acid (cf. Krannichfeldt, *Ber.*, 1914, **47**, 156).



*p*-Acetoxybenzoic acid was subjected to the Fries migration under different conditions as before. Since the *para* position is occupied, the acetyl group could be expected to go only to the *ortho* position to the hydroxyl group. The migration product has been assigned the constitution 3-acetyl-4-hydroxybenzoic acid (IV) as it dissolves in sodium bicarbonate solution and is

precipitated on acidifying; it gives red colour with alcoholic ferric chloride indicating the *ortho* position of -OH and -COCH<sub>3</sub> groups; it gives ester, oxime and semicarbazone confirming the presence of carboxyl and ketonic groups; it gives a chalcone on condensation with benzaldehyde in presence of alkali.



The Fries migration of 3-acetoxybenzoic acid was tried under various conditions but in all cases the unchanged *m*-hydroxybenzoic acid was recovered; in no case the migration product could be obtained. Thus, it is evident that the carboxyl group in the *meta* position to hydroxyl group hinders the migration (cf. Mauthner, *J. prakt. Chem.*, 1933, ii, **136**, 205).

#### EXPERIMENTAL

For the migration of *o*-acetoxybenzoic acid, the aspirin used in this investigation was of extra pure quality, m.p. 135° and did not give any coloration with ferric chloride.

*p*-Acetoxybenzoic acid (m.p. 189°) was prepared by acetic anhydride-pyridine method as it was found to give consistently better yield of the pure derivative.

*m*-Acetoxybenzoic acid (m.p. 129-30°) was prepared by acetic anhydride-concentrated sulphuric acid method.

The migration was carried out (a) without a solvent and (b) in nitrobenzene as a solvent according to the general method already described in the earlier papers (*loc. cit.*). In each case, several experiments were repeated for the purpose of confirmation. The Fries migration of aspirin in presence of nitrobenzene as a solvent, as well as without it, has been investigated under various conditions of temperature and period of heating. Similarly the migration of *p*-acetoxybenzoic acid was investigated. For sake of uniformity in all experiments 3g. (1 mol.) of the acetoxy-acid was taken and the weights of the products mentioned are of pure products after necessary crystallisation. The migrations were also studied using different proportions of aluminium chloride (1.1, 2.2, 3.3 mols.) and by varying time and temperature of the reaction. To avoid repetition, these experiments have been omitted from the experimental; only the experiments under the optimum condition are described.

#### Fries Migration of Aspirin : Formation of 5-Acetyl-2-hydroxybenzoic Acid

(a) *In presence of a Solvent.*—To a solution of anhydrous aluminium chloride (7g., 3.3 mols.) in dry nitrobenzene (35 c.c.) powdered aspirin (3g., 1 mol.) was added at once. A vigorous reaction set in and HCl fumes were copiously evolved. The reaction mixture was left for one hour at room temperature, protected by a CaCl<sub>2</sub> guard tube to prevent access of moisture, with occasional shaking. Ice and HCl (conc., 5 c.c.) were then added and the mixture was steam-distilled to remove nitrobenzene. The hot residual liquid was filtered through a hot water funnel. The filtrate on cooling deposited white needles, yield 2.5 g. It was crystallised from dilute alcohol, m.p. 216°-17° (mixed m.p. with the product obtained by Friedel-Crafts acetylation of salicylic acid). (Found: C, 59.7; H, 4.2; equiv., 178.6. C<sub>9</sub>H<sub>6</sub>O<sub>4</sub> requires C, 60.0; H, 4.44 per cent.



Equiv., 180). The acid gives wine-red colour with alcoholic ferric chloride. It is soluble in hot water, alcohol; insoluble in chloroform and benzene.

(b) *Without a Solvent*.—The reactants in the same proportions as above were intimately mixed and heated for one hour on an oil-bath at 120°-125° with calcium chloride guard tube. It was then cooled; ice and concentrated HCl added and the solid separating was collected and crystallised from dilute alcohol in needles, m.p. 216°-17°, yield 1.3g. (the mixed melting point with the above product was unchanged).

The *oxime*, prepared as usual, melted at 180-81° (decomp.). The *semicarbazone* crystallised from alcohol, m.p. 283-84 (decomp.).

*2-Hydroxy-5-ethylbenzoic Acid*.—The keto-acid (2g.) was reduced according to Clemmensen by using zinc amalgam (10 g.) and hydrochloric acid (1 : 1, 25 c.c.). The hot reaction mixture was filtered; on cooling the filtrate, the reduction product came down; it was crystallised from alcohol in small needles, m.p. 122-23. It gives blue colour with alcoholic ferric chloride. (Found : C, 64.9; H, 5.8; equiv., 165.9. Calc. for  $C_9H_{10}O_3$ : C, 65.0; H, 6.0 per cent. Equiv., 166).

*3-Carboxy-4-hydroxychalkone*.—To the mixture of the keto-acid (1g.) dissolved in alcohol (10 c.c.) and benzaldehyde (2c.c.) potassium hydroxide (10<sup>0</sup>., 10 c.c.) was added slowly and the mixture left overnight. It was then diluted with cold water and acidified with hydrochloric acid. The solid was collected and crystallised from alcohol as yellow needles, m.p. 238 (decomp.). It gives red colour with conc.  $H_2SO_4$  and dissolves in sodium bicarbonate solution with effervescence. (Found : C, 71.2; H, 4.2.  $C_{16}H_{12}O_4$  requires C, 71.65; H, 4.48 per cent).

*Fries Migration of 4-Acetoxybenzoic Acid : Formation of 3-Acetyl-4-hydroxybenzoic Acid*

An intimate mixture of aluminium chloride (7g., 3.3 mols.) and 4-acetoxybenzoic acid (3g., 1 mol.) was heated on an oil-bath at 156-155° for one hour in a flask protected from moisture by a  $CaCl_2$  guard tube during heating. HCl fumes were evolved. It was then cooled, treated with ice and HCl; the solid separating was collected and crystallised from alcohol, m.p. 240-41, yield 1.7g. It gives red colour with alcoholic ferric chloride. (Found : Equiv., 178.8.  $C_9H_8O_4$  requires equiv., 180).

The migration was carried out at 180-185° without any difference in the amount of the migration product obtained. If, however, nitrobenzene was used as a solvent, no migration product could be obtained.

The *oxime* crystallised from alcohol, m.p. 259-60° (decomp.). The *semicarbazone*, sparingly soluble in most of the common organic solvents, did not melt up to 260°.

The *ethyl ester*, prepared by refluxing the acid and ethyl alcohol in presence of a few drops conc. sulphuric acid on a water-bath for nearly 21 hours, crystallised from alcohol in needles, m.p. 71°. (Found : C, 63.55; H, 5.1.  $C_{11}H_{12}O_4$  requires C, 63.8; H, 5.2 per cent).

*2-Hydroxy-5-carboxychalkone* was prepared as before. It crystallised from acetic acid as bright yellow needles, m.p. 222° (decomp.). (Found : C, 71.5; H, 4.1.  $C_{16}H_{12}O_4$  requires C, 71.65; H, 4.5 per cent).

It gives red colour with conc. sulphuric acid and reddish brown colour with alcoholic ferric chloride.

The results show that three molecules of aluminium chloride are required for the acetyl group to migrate, while with lesser amounts of the same, the cleavage products are formed. The

amount of the deacetylated product increases as the amount of aluminium chloride is decreased. In case of *m*-hydroxybenzoic acid, even with the above proportions or more of the aluminium chloride, no migration could be effected.

In the migration of aspirin in the presence of a solvent, the room temperature is favourable to the migration as the yield of the migration product is good and the reaction is smooth. At higher temperatures, more of the deacetylated product was formed than the product by migration. If the reaction was carried out without a solvent, the same product was obtained in lesser yields; there is no appreciable effect of temperature on the course of the reaction.

In the case of *p*-acetoxybenzoic acid, no migration product is obtained in presence of nitrobenzene as a solvent even though different temperatures are used. But only a white light product of high melting point is obtained. When no solvent is used and the temperature is varied, the migration product is obtained within a range of 150 -180°. It is noteworthy that below 120° no migration takes place; whereas, in case of aspirin, it is best effected at ordinary temperature in presence of a solvent.

The large-scale experiments under the best conditions mentioned above have been tried and good yields of the ketonic acids have been obtained. The results clearly show that the carboxyl group in the *ortho* or *para* position to the hydroxyl group does not retard or inhibit the migration; whereas, it in the *meta* position inhibits it.

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## PERIODIC ACID AND PERIODATES. PART I. SOLUBILITY OF PERIODIC ACID IN WATER

By P. P. GYANI AND B. P. GYANI

The solubility of periodic acid in water at temperatures between 0° and 45° has been determined. The heat of solution of the acid in a saturated solution has been calculated from these data. It is found that the process is endothermic, the thermal change being small and about of the same order as observed in mixing acetic acid with small quantities of water in a calorimeter. There is some indication that the acid may exist in two forms differing in water content, the probable transition temperature being 29.5°.

Practically no quantitative data for the solubility of periodic acid have appeared in literature. According to Langlois (*Ann. chim. phys.*, 1852, **34**, 257) periodic acid is slightly soluble in alcohol, less soluble in ether, and very soluble in water. Hill (*J. Amer. Chem. Soc.*, 1928, **50**, 2678) has mentioned that the solubility of periodic acid at room temperature is about 53%. This figure was obtained after analysing the mother-liquor after the crystallisation of periodic acid, and therefore it may be only approximate. Moreover, the temperature is not defined precisely. Willard ("Inorganic Synthesis", Vol. I, p. 173, McGraw Hill Book Co., London, 1939) gives the following figures (Table I) for the solubility of periodic acid in concentrated nitric acid of sp. gr. 1.42.

TABLE I

Temperature,	H <sub>5</sub> IO <sub>6</sub> (g. 100 c.c.)	H <sub>2</sub> O (g. per 100 g. soln.)
12±1	5.68	3.95
26±0.05	7.82	5.11

He further mentions that the solubility rises rapidly above 25° and is about ten times as much in water as in concentrated nitric acid. It is therefore clear that no systematic attempt at measuring the solubility of periodic acid in water at different temperatures has been made. Nevertheless, such a study might be valuable in deciding whether or not different periodic acids exist in contact with their saturated solutions at different temperatures.

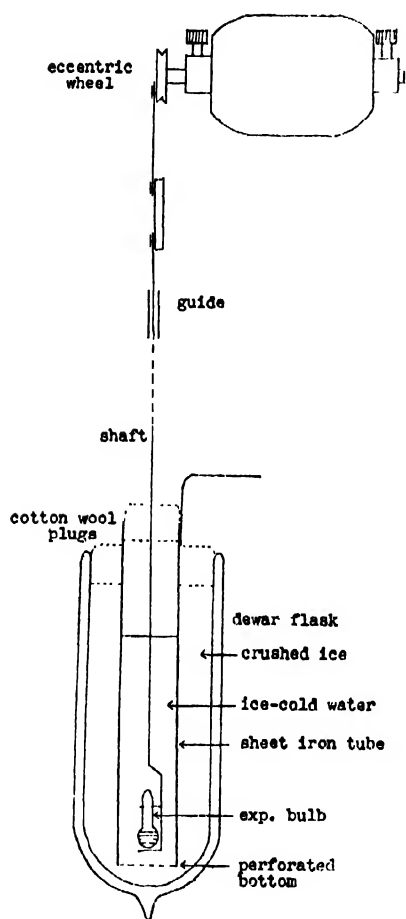
### EXPERIMENTAL

The periodic acid was prepared by oxidation of sodium iodate in solution by potassium persulphate, as described by Booth ("Inorganic Synthesis", Vol. I, p. 168).

Two different methods were employed to estimate the periodic acid. The first, due to Partington and Bahl (*J. Chem. Soc.*, 1934, 1086) depends on the liberation of iodine from potassium iodide under specified conditions. The second, due to Müller and Friedberger (*Ber.*, 1902, **35**, 2665), also makes use of the same reaction but under different conditions; under these conditions iodic acid and iodates do not liberate iodine. The two methods were found to check each other closely.

The experimental arrangement for the determination of solubility consisted of a small bulb of about 10c.c. capacity blown out of pyrex glass tubing. A little water and excess of periodic acid were introduced into it and the stem of the bulb was sealed off. It was then immersed in a water thermostat and shaken mechanically. Shaking was stopped after 48 hours and the tube was allowed to stand another 24 hours for the solid to settle down. The clear solution was then taken out and analysed. Solubility measurements at various temperatures were made. The thermostat used for all the temperatures, except 0° and 20°, was an ordinary electrically maintained one with a maximum temperature variation of 0.05°. For 0°, the self-explanatory arrangement shown in Fig. 1 was used. By this arrangement the temperature could be maintained at

FIG. 1.

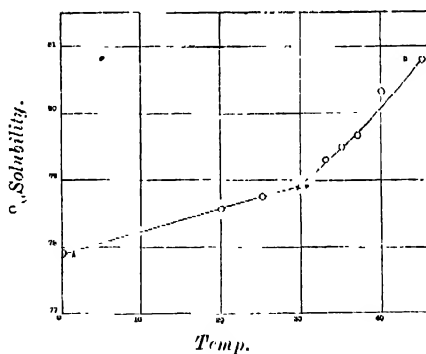


0° for about 3 days with a single charge of ice during winter. The water inside the cylinder showed a maximum variation in temperature of 0.2°. For a temperature of 20°, the same arrangement was used, but instead of taking ice in the Dewar vessel water at 20° was taken. By adding a few pieces of ice occasionally the temperature could be maintained at 20°.

TABLE II

Temp.	..	0°	20°	25	33°	35°	37°	40°	45°
Acid, $\text{HIO}_4$ $2\text{H}_2\text{O}$ contained in 100 g. of sat. soln in g.	..	77.91	78.57	78.74	79.32	79.50	79.66	80.30	80.78

FIG. 2

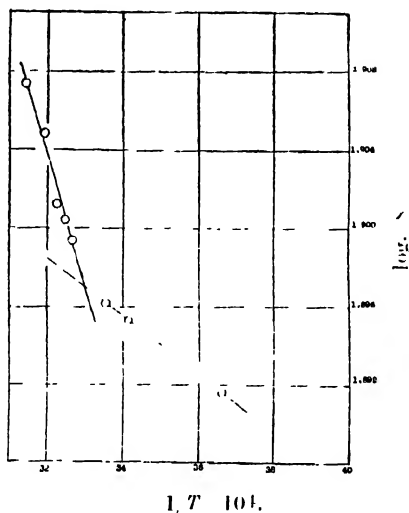


## DISCUSSION

The results obtained from these measurements are recorded in Table II. The data are shown graphically in Fig. 2 in which the solubility has been plotted against the corresponding temperature. The experimental points are found to lie on two distinct lines AP and BP which are almost straight and intersect at the point P. This point corresponds to a temperature of about 29.5°. Below this temperature the solubility increases at the rate of about 0.03 g. per degree; above P it increases at the rate of about 0.12 g. per degree, that is to say, about four-fold as rapidly.

These facts lend support to the possibility that AP and BP may be the solubility curves of two different forms of the acid, probably differing in water content. P should then be the transition point for the two forms. Incidentally, the present experiments support the previously recorded qualitative fact that the solubility of periodic acid increases rapidly above 25°.

FIG. 3



It is possible to calculate with the help of the present data the approximate heats of solution of the two forms. For this purpose the equation

$$\ln \frac{S_2}{S_1} = \frac{\mathcal{L}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

may be used. Here  $S_1$ ,  $S_2$  are the solubilities of the substance at the absolute temperatures  $T_1$ ,  $T_2$  respectively and  $\mathcal{L}$  is the calorimetric heat of solution in a saturated solution (cf. Partington, "Thermodynamics", p. 305, London, 1913). Although this equation is not universally accepted (*Brit. Chem. Abs.*, 1888, ii, 552 ; 1899, ii, 11,545) it has been frequently used to calculate  $\mathcal{L}$  from observed solubilities at different temperatures. Obviously, average values of  $\mathcal{L}/R$  may be obtained by plotting the logarithm of solubility against the inverse of the absolute temperature and measuring the slopes of the resulting curves. This has been shown in Fig. 3. It is found that the graphs are practically straight lines showing that there is no sensible variation in the value of  $\mathcal{L}$  for each form in the range of measurements. The values of  $\mathcal{L}$  have been calculated from these slopes and come out to be about 69 and 298 cal. per mole respectively for the two forms below and above 29.5°. These values may be compared with 6857 cal. for succinic acid—water at 5° and 6500 cal. for *o*-nitrobenzoic acid—water at 20°. Potassium perchlorate has a heat of solution of 12300 cal. (Noyes and Sammet, *Z. physikal. Chem.*, 1903, **43**, 513). Obviously the heat of solution of periodic acid is small in comparison with these values although heat is absorbed in each case. It may probably be compared to the heat of solution of acetic acid in water studied by Thomsen ; in these measurements the acid was mixed with different proportions of water and the heat evolved measured in a calorimeter. Thomsen found that one mole of the acid mixed with half a mole of water brought about an absorption of 130 cal. of heat (Landolt-Börnstein's Tables, p. 885, Berlin, 1912), but he did not appear to have studied the thermal effect at differ-

ent temperatures. He, however, obtained much variation in the measured heat as the proportion of water was increased, the process of solution becoming exothermic at 20 moles of water and above. The heat of solution with different proportions of water at a constant temperature therefore deserves investigation in the case of periodic acid also, and is proposed to be taken up later.

The authors wish to thank Principal P. B. Ganguly and Professor M. Q. Doja for their kind interest in this investigation. One of us (P. P. G.) is also grateful to the Patna University for the award of a research scholarship.

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## SEARCH FOR INSECTICIDES. PART II

By A. B. SEN AND P. M. BHARGAVA

Trichloroacetates of *o*-chlorophenol, *m*-chlorophenol, catechol, resorcinol and hydroquinone have been prepared.

It is necessary to have a grouping which confers lipoid solubility and another one possessing toxicity, in the molecule of a good contact insecticide (Busvine, *Nature*, 1945, **156**, 179). A number of esters of trichloroacetic acid and halogenated phenols have been prepared with this aim in view (Sen and Bhargava, this *Journal*, 1948, **25**, 277). In this paper, the preparation of trichloroacetates of *o*-chlorophenol, *m*-chlorophenol, catechol, resorcinol and hydroquinone have been described. The trichloroacetyl esters of *o*- and *m*-chlorophenols are colorless liquids and are obtained in nearly theoretical yields. The di-trichloroacetates of resorcinol, catechol and hydroquinone are not obtained in so good yields; these esters darken on exposure to light and the last two are very hygroscopic.

### EXPERIMENTAL

*Preparation of the Sodium Salts of the Phenols.* The sodium salts of *o*-chlorophenol, *m*-chlorophenol, catechol and hydroquinone were prepared by adding an absolute alcoholic solution of the phenol to a solution of sodium ethoxide (equimolecular quantity) in absolute alcohol (15 c.c. for each g. of sodium). In the case of catechol and hydroquinone, the sodium salts separated out as crystalline precipitates, which were quickly filtered off, pressed and dried. In the case of *o*- and *m*-chlorophenols, the sodium derivatives could only be obtained after distilling off the excess of alcohol on an oil-bath at 125–130°.

The sodium salt of resorcinol was prepared by adding a little less than the required amount of caustic soda, dissolved in a small quantity of water, to resorcinol, using phenolphthalein as the indicator. The solution was evaporated almost to dryness on a water-bath and left in a vacuum desiccator.

*Condensation with Trichloroacetyl Chloride.* The sodium salt of the phenol was suspended in dry petrol-ether (40–50 c.c.) in a 250 c.c. pyrex flask attached to a reflux condenser; the flask was then cooled in ice and trichloroacetyl chloride ( $1\frac{1}{2}$  to 2 times the calculated amount) added from the top of the condenser. The reaction was allowed to take place for  $\frac{1}{2}$  to 1 hour in the cold; the contents of the flask were then refluxed over a water-bath for 2 to 3 hours and then left overnight. The sodium chloride formed was filtered off and well washed with petrol-ether. The petrol-ether was removed from the filtrate on a water-bath and the residual liquid distilled in vacuum on a metal-bath, when the trichloroacetate of the corresponding phenol was obtained. The trichloroacetates of *m*- and *o*-chlorophenols and the di-trichloroacetates of catechol, hydroquinone and resorcinol, thus prepared, are described in Table I.

TABLE I.

No.	Reactants		B. p. of the ester.	Yield.	Properties.	Formula.	Found (%)			Calculated (%)		
	Na salt of phenol.	$\text{CCl}_3\text{COCl}$ .					C.	H.	Cl.	C.	H.	Cl.
I	10 g.	18 g.	86-88 / 22mm.	15 g	Colorless liquid	$\text{C}_8\text{H}_4\text{O}_2\text{Cl}_4$	34.77	1.45	51.52	35.04	1.46	51.83
II	5	9	119-122 / 26	9	Colorless liquid	$\text{C}_8\text{H}_4\text{O}_2\text{Cl}_4$	34.87	1.49	51.59	35.04	1.46	51.83
III	4.4	9	169-171	18	8 Pale yellow liquid, solidifying on cooling in ice. Has a characteristic smell and turns deep green on keeping.	$\text{C}_{10}\text{H}_4\text{O}_4\text{Cl}_6$	29.62	1.16	53.40	29.92	1.00	53.16
IV	7.7	18.2	95-5	8	Colorless liquid solidifying to white crystals on cooling in ice. Has very characteristic smell and turns deep brown on keeping, is very hygroscopic.	$\text{C}_{10}\text{H}_4\text{O}_4\text{Cl}_6$	29.67	1.06	53.01	29.92	1.00	53.16
V	6.6	18.2	95-5	6.4	Colorless liquid with characteristic smell, turns red and then brown in a few months	$\text{C}_{10}\text{H}_4\text{O}_4\text{Cl}_6$	29.56	1.08	52.79	29.92	1.00	53.16

I Trichloroacetate of *o*-chlorophenol II Trichloroacetate of *m*-chlorophenol III Ditrichloroacetate of catechol.  
 IV Ditrichloroacetate of hydroquinone V Ditrichloroacetate of resorcinol

The hydrolysis of the trichloroacetate of *o*-chlorophenol by alkali resulted in the formation of *o*-chlorophenol and trichloroacetic acid.

The insecticidal action of the compounds described in this paper, is under investigation.

One of the authors (P. M. B.) is indebted to the U. P. Government for award of a research scholarship for carrying out this work.



## NITRATION OF SOME COUMARIN DERIVATIVES

BY A. R. NAIK AND G. V. JADHAV

7-Hydroxy-3:4-dimethylcoumarin, its methyl ether and 7-hydroxy-8-acetyl-4-methylcoumarin have been nitrated and their nitro derivatives obtained.

Nitration of 7-hydroxy-3:4-dimethylcoumarin gave 8-nitro derivative (Chakravarti and Ghosh, *J. Indian Chem. Soc.*, 1935, **12**, 622). It is now found that this coumarin gives a dinitro derivative, 7-hydroxy-3:4-dimethyl-6:8-dinitrocoumarin, if nitration is allowed to proceed at higher temperature for a short time, and 2:4-dihydroxy-3:5-dinitroacetophenone, if the nitration is allowed to proceed for a long time. Its methyl ether and acetyl derivative have been prepared. The nitration of its methyl ether either in sulphuric acid or acetic acid gives the same mononitro derivative. As the melting point of this nitro compound is different from that of 7-methoxy-3:4-dimethyl-8-nitrocoumarin, it is given the constitution as 7-methoxy-3:4-dimethyl-6-nitrocoumarin. The nitration of 7-hydroxy-8-acetyl-4-methylcoumarin at room temperature and for a short time gives 3-nitro- and 6-nitro-coumarins. Their methyl ether and phenylhydrazone derivatives have also been prepared.

Prolonged nitration or nitration at higher temperature gives 7-hydroxy-4-methyl-3:6:8-trinitrocoumarin.

### EXPERIMENTAL

*7-Hydroxy-3:4-dimethyl-6:8-dinitrocoumarin.*—7-Hydroxy-3:4-dimethylcoumarin (5 g.) was suspended in glacial acetic acid (50 c.c.) and nitric acid (*d* 1.42, 5 c.c.) was gradually added to it and the reaction mixture was then warmed on a boiling water-bath until the solid went into solution. Yellow needles, separated on cooling, crystallised from alcohol, m.p. 210–11°. More solid was obtained on diluting the original mother-liquor. Alcoholic ferric chloride gave blood-red coloration with the substance. (Found: N, 10.21.  $C_{11}H_8O_7N_2$  requires N, 10.0 per cent).

*7-Methoxy-3:4-dimethyl-6:8-dinitrocoumarin.*—Sodium salt of the above dinitrocoumarin was prepared by adding 25% solution of sodium hydroxide to its suspension in absolute alcohol and the precipitated salt washed with absolute alcohol and dried at 140°.

The dried sodium salt (1 g.) was suspended in toluene (30 c.c.), dried over Na, and dimethyl sulphate (1.5 c.c.) added to it and the mixture heated at 120° for about 6 hours. The mixture was then mixed with water and subjected to steam distillation. The residue was washed with alkali and finally crystallised from alcohol in pale yellow needles, m.p. 141°. It gave no characteristic coloration with alcoholic ferric chloride solution. (Found: N, 9.6.  $C_{12}H_{10}O_7N_2$  requires N, 9.5 per cent).

*7-Acetoxy-3:4-dimethyl-6:8-dinitrocoumarin.*—The above dinitrocoumarin was acetylated by boiling for 3 hours with acetic anhydride in presence of pyridine. It crystallised from benzene in short yellow needles, m.p. 200–201°. (Found: N, 8.9.  $C_{13}H_{10}O_8N_2$  requires N, 8.7 per cent).

*2:4-Dihydroxy-3:5-dinitroacetophenone.*—7-Hydroxy-3:4-dimethyl-6:8-dinitrocoumarin (1 g.) was dissolved in acetic acid (15 c.c.), nitric acid (*d* 1.42, 4 c.c.) added and the mixture heated on a boiling water-bath for 1 hour. Yellow cubes separated on cooling the mixture in a refrigerator, m.p. 169°. (Found: N, 11.7.  $C_8H_6O_7N_2$  requires N, 11.6 per cent).

The same substance was also obtained from 7-hydroxy-3:4-dimethylcoumarin by nitrating it in acetic acid solution with excess of nitric acid on a boiling water-bath.

*7-Methoxy-3:4-dimethyl-6-nitrocoumarin.*—7-Methoxy-3:4-dimethylcoumarin (2 g.) was dissolved in sulphuric acid (7 c.c.). To ice cooled solution a mixture of nitric acid (1 c.c.) and sulphuric acid (4 c.c.) was added dropwise with constant stirring. It was kept at that temperature for about half an hour and then poured over crushed ice, and the solid obtained was crystallised

from acetic acid in straw-yellow needles, m.p. 232-33°. (Found : N, 5.9.  $C_{12}H_{11}O_5N$  requires N, 5.6 per cent).

Nitration of the coumarin in acetic acid medium on a boiling water-bath for about an hour and a half gave the same substance.

**7-Methoxy-3 : 4-dimethyl-8-nitrocoumarin.**—7-Hydroxy-3 : 4-dimethyl-8-nitrocoumarin (1 g.), dissolved in dry acetone (100 c.c.), was mixed with methyl iodide (6 c.c.) and anhydrous potassium carbonate (3g.) and boiled for 24 hours. The residue left after the removal of the solvent was washed with very dilute sodium hydroxide solution and finally crystallised from alcohol in straw-yellow needles, m.p. 218-20°. (Found : N, 5.8.  $C_{12}H_{11}O_5N$  requires N, 5.6 per cent).

**7-Hydroxy-8-acetyl-4-methyl-3-nitrocoumarin.** 7-Hydroxy-8-acetyl-4-methylcoumarin (5 g.) suspended in acetic acid (35 c.c.) was treated with nitric acid ( $d$  1.42, 20 c.c.) and the reaction mixture was left at room temperature. After about an hour crystals began to separate which were filtered after half an hour more. (The mother-liquor was worked up separately). The substance was then washed with dilute sodium bicarbonate solution and the solid finally crystallised from alcohol in silky needles, m.p., 217-18°. It gave red coloration with alcoholic ferric chloride solution. (Found : N, 5.3.  $C_{12}H_9O_6N$  requires N, 5.3 per cent).

Its phenylhydrazone crystallised from acetic acid in orange-yellow needles, m.p. 271-72° (decomp.). (Found : N, 12.1.  $C_{18}H_{15}O_5N_3$  requires N, 11.9 per cent).

**2 : 4-Dihydroxy-3-acetylacetophenone.** 7-Hydroxy-8-acetyl-4-methyl-3-nitrocoumarin (1 g.) was dissolved in liquor ammonia (40 c.c.) and the solution heated on a boiling water-bath for about 2 hours. It was then acidified and subjected to steam distillation when 2 : 4-dihydroxy-3-acetylacetophenone was obtained as white needles in the distillate, m.p. 87°. It showed no lowering in melting point when mixed with a genuine specimen.

**7-Methoxy-8-acetyl-4-methyl-3-nitrocoumarin.**—This was obtained by methylating the hydroxy compound with methyl iodide in dry acetone medium in presence of anhydrous potassium carbonate. It crystallised from alcohol in yellow needles, m.p. 208-209°. (Found : N, 5.3.  $C_{13}H_{11}O_6N$  requires N, 5.1 per cent).

**7-Hydroxy-8-acetyl-4-methyl-6-nitrocoumarin.**—The mother-liquor from the 3-nitro isomer was diluted with water, when a solid separated. It was warmed with ammonium hydroxide solution and the orange-red filtrate was acidified with dilute hydrochloric acid and the solid obtained crystallised from acetic acid in yellow clusters of needles, m.p. 203-204°. It gave red coloration with alcoholic ferric chloride solution. (Found : N, 5.4.  $C_{12}H_9O_6N$  requires N, 5.3 per cent).

Its phenylhydrazone crystallised from acetic acid in clusters of orange needles, m.p. 230-31° (decomp.). (Found : N, 12.0.  $C_{18}H_{15}O_5N_3$  requires N, 11.9 per cent).

**7-Methoxy-8-acetyl-4-methyl-6-nitrocoumarin.**—It was obtained by methylating the hydroxy compound by methyl iodide in acetone solution in presence of anhydrous potassium carbonate. It crystallised from dilute alcohol in pale yellow needles, m.p. 125°. (Found : N, 5.3.  $C_{13}H_{11}O_6N$  requires N, 5.1 per cent).

**7-Hydroxy-4-methyl-3 : 6 : 8-trinitrocoumarin.**—7-Hydroxy-8-acetyl-4-methylcoumarin (1 g.), suspended in acetic acid (8 c.c.), was treated with nitric acid ( $d$  1.42, 4 c.c.). After about an hour yellow needles began to separate. The mixture was left overnight at room temperature and yellow cubes were filtered and recrystallised from acetic acid, m.p. 225-26° (decomp.). (Found : N, 13.7.  $C_{10}H_5O_9N_3$  requires N, 13.5 per cent).

The same substance was obtained by heating the reaction mixture on a boiling water-bath for half an hour.

## CONDUCTANCE OF CALCIUM GLUCONATE SOLUTIONS

BY A. N. KAPPANNA AND INDRA DEVA ARYA

Conductivities of calcium gluconate solutions have been determined over the temperature range of 25° to 50° and the range of equivalent concentration 0.10 to 0.002. The ionic conductivities of the gluconate ion at different temperatures have been calculated. Square root of equivalent concentration plotted against equivalent conductivities give very good straight lines in dilute solutions but the slopes differ considerably from the calculated Onsager slopes.

The prominence attained by calcium gluconate in pharmacology and pharmaceutical industry calls for a thorough understanding of the physicochemical properties of the salt. In connection with other work in progress in this laboratory it became necessary to know the conductivities of calcium gluconate solutions. The only record we have been able to trace in literature is that of a few measurements by Jensen and Ungast (*J. Chem. Phys.*, 1941, **9**, 195). We have measured the conductivities of the salt over the temperature range of 25°-50° and in dilute solutions. The results are recorded in the present communication.

## EXPERIMENTAL

Pure calcium gluconate was subjected to recrystallisation thrice, the final purification being effected from solutions in conductivity water. Analysis of the compound showed it to be the monohydrate.

Conductivity water as well as solutions of the salt were prepared and preserved carefully. Conductivity measurements were carried out with precision equipment using a 1000 cycle symmetric A. C. The conductivity of the water used for the preparation of each solution was measured and the solvent correction applied. The cell constant was determined frequently and checked up. The thermostat maintained the requisite temperature constant within  $\pm 0.05^\circ$ . The usual precautions have all been observed. Repeated measurements were made for each solution, the solution itself being prepared fresh for each measurement. We estimate the error in our measurements to be in the neighbourhood of  $\pm 1\%$ . Extra-ordinary accuracy is not therefore claimed for our results.

Table I gives the results of our measurements at different temperatures.

TABLE I  
*Equivalent conductivity.*

Eq. conc.	25°.	30°.	35°.	40°.	45°.	50°.
0.10	28.61	33.05	38.16	40.18	44.17	50.85
0.05	37.36	42.54	50.04	54.96	60.72	68.24
0.02	51.05	59.00	63.25	69.35	78.20	88.90
0.01	57.48	64.98	72.72	81.47	88.20	102.20
0.005	66.82	73.20	81.08	91.52	99.38	114.98
0.002	72.85	80.20	90.05	102.00	109.65	127.00
0.001	76.53	84.20	94.10	106.70	115.00	132.80
0.0005	78.20	86.90	97.40	110.50	118.90	136.40
0.0002	80.70	89.45	100.20	113.50	124.40	139.55
	84.80	94.50	105.00	116.70	128.90	143.00

Our results at 25° differ considerably from those of Jensen and Ungast (*loc. cit.*).

Equivalent conductivities plotted against square root of eq. concentration even up to concentration of  $0.01N$  give very good straight lines. This is rather surprising when we take into consideration the large variations in conductivities at all the temperatures, as we proceed from  $c=0.01$  to  $0.0002$ , the increase amounting to near about 50%. This kind of variation is indicative of incomplete dissociation. The values  $\Lambda_{\infty}$  in the bottom column of the table have been obtained by the graphical method extending the straight lines up to  $\sqrt{c}=0$ .

Table II contains the calculated values for the mobilities of gluconate ion at different temperatures. The values for the  $\frac{1}{2}\text{Ca}^{++}$  mobilities have been taken from the work of Benson and Gordon on the conductance of  $\text{CaCl}_2$  solutions (*J. Chem. Phys.*, 1945, **13**, 470). (The value for  $50^\circ$  was obtained by extrapolation).

TABLE II

	25°.	30°.	35°.	40°.	45°.	50°.
$\Lambda_{\infty}$ ..	84.80	94.50	105.0	116.70	129.90	143.00
$\Lambda_{\frac{1}{2}\text{Ca}^{++}}$	59.50	66.60	73.26	80.03	88.21	93.50
Gluconate ion	25.30	27.90	31.74	36.67	41.69	49.50
Onsager slope, calc.	158.7	177.5	193.7	217.6	244.00	268.00
Onsager slope, expt.	266	295	318	372	399	437

In an electrolyte, where the variation of conductivity with concentration in dilute solutions is great, there is hardly any justification in expecting agreement with Onsager equation. The figures in the last two horizontal rows are included, as the differences between the calculated values and observed values for Onsager slopes are very wide.

In Table III the ionic conductances of organic ions are compared with that of gluconate ion.

TABLE III

Ion.	No. of atoms.	Conduc. at 25°.	Ion.	No. of atoms.	Conduc. at 25°.
Formate	4	51.2	Butyrate	13	30.8
Acetate	7	38.3	Valerate	16	28.8
Propionate	10	34.3	Caproate	19	27.4
			Gluconate	25	26.5

The values for other ions are taken from Landolt's Tables.

## BROMINATION OF ACETYLURETHANE AND ACETYL-SUBSTITUTED UREAS

By C. M. DESAI AND M. N. DESAI

Acetyl-phenyl, -*o*-tolyl, -*m*-tolyl, -*p*-tolyl, - $\alpha$ -naphthyl, - $\beta$ -naphthyl, -*p*-xylyl, -*o*-anisyl, -*p*-phenetyl and -*m*-phenetyl carbamides and acetylurethane have been brominated and the constitution of bromo derivatives so obtained has been established by synthesis.

Extensive work has been done on halogenation and replacement of halogens by hydrogen in compounds containing -CO-CH<sub>2</sub>-CO- grouping (Whiteley, *J. Chem. Soc.*, 1924, 710 ; 1925, 743 ; Naik *et al.*, *J. Indian Chem. Soc.*, 1913, **20**, 355, 365, 431). Bromination of compounds containing -CO-NH-CO- grouping has been studied in this paper on acetyl-phenyl, -*o*-tolyl, -*m*-tolyl, -*p*-tolyl, - $\alpha$ -naphthyl, - $\beta$ -naphthyl, -*p*-xylyl, -*o*-anisyl, -*p*-phenetyl and -*m*-phenetyl carbamides and acetylurethane and it has been found that bromine enters only the nucleus in phenyl-substituted ureas and only the methyl group in acetylurethane. The constitution of the halogen derivatives so obtained has been established by synthesising the same compounds from the corresponding amino derivatives and acetylurethane.

### EXPERIMENTAL

*Substituted Carbamides.*—The acetyl derivatives of substituted carbamides were obtained from acetylurea and amino compounds by heating them on an oil-bath at 160° with an air condenser when ammonia was evolved and the reaction completed in about 3 hours. The products were treated with water, dried and crystallised from alcohol or ethyl acetate. The compounds so obtained are identical with those prepared from acetylurethane and the corresponding amino compounds. Acetyl-*m*-phenetylcarbamide, m.p. 162-65°. (Found : N, 12.2. C<sub>11</sub>H<sub>14</sub>O<sub>3</sub> N<sub>2</sub> requires N, 12.61 per cent).

Acetyl-*o*-phenetylcarbamide, m.p. 212-13°.

Acetyl-*o*-anisylcarbamide, m.p. 194-95°.

Acetyl-*p*-xylylcarbamide, m.p. 172-73°.

On hydrolysis with potassium hydroxide solution on a water-bath for half an hour, acetyl group was removed and the free substituted carbamides obtained and crystallised from aqueous alcohol.

*o*-Phenetylcarbamide, m.p. 135-36°. (Found : N, 15.3. C<sub>9</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub> requires N, 15.55 per cent).

*p*-Anisylcarbamide, m.p. 162-63°. (Found : N, 16.38. C<sub>8</sub>H<sub>10</sub>O<sub>2</sub>N<sub>2</sub> requires N, 16.86 per cent).

*p*-(1 : 4 : 5)-Xylylcarbamide, m.p. 209-10°, resolidifying and decomposing rapidly above 275°. (Found : N, 16.5. C<sub>9</sub>H<sub>12</sub>ON<sub>2</sub> requires N, 17.01 per cent).

*Bromo Derivatives.*—The substituted carbamide (1 g.) was suspended in carbon tetrachloride in a flask and bromine in excess was added slowly. After the addition was over, the contents were refluxed for about 3 hours, cooled, filtered, washed with benzene and crystallised from alcohol. They are white crystalline solids, insoluble in water, soluble in hot alcohol, and sparingly in hot benzene.

Acetyl-4-bromophenylcarbamide, m.p. 218-19°. (Found : N, 11.11 ; Br, 31.05. C<sub>9</sub>H<sub>9</sub>O<sub>2</sub>N<sub>2</sub>Br requires N, 10.9 ; Br, 31.12 per cent).

Acetyl-5-bromotolylcarbamide, m.p. 226-28°. (Found : N, 10.39 ; Br, 28.93.  $C_{10}H_{11}O_2N_2Br$  requires N, 10.33 ; Br, 29.52 per cent).

Acetyl-4 : 6-dibromo-*m*-tolylcarbamide, m.p. 215-17°. (Found : N, 8.45 ; Br, 45.5.  $C_{10}H_{10}O_2N_2Br_2$  requires N, 8.0 ; Br, 45.7 per cent).

Acetyl-3-bromo-*p*-tolylcarbamide, m.p. 226-28°. (Found : N, 10.26 ; Br, 28.0.  $C_{10}H_{11}O_2N_2Br$  requires N, 10.33 ; Br, 29.5 per cent).

Acetyl-4-bromo- $\alpha$ -naphthylcarbamide, blackening at 235-40 and melting at 258-60°. (Found : N, 9.07 ; Br, 27.0.  $C_{13}H_{11}O_2N_2Br$  requires N, 9.16 ; Br, 26.05 per cent).

Acetyl-1-bromo- $\beta$ -naphthylcarbamide, m.p. 226-28°. (Found : N, 9.21 ; Br, 25.3.  $C_{13}H_{11}O_2N_2Br$  requires N, 9.17 ; Br, 26.05 per cent).

Acetyl-2-bromo-(1 : 4 : 5)-xylylcarbamide, m.p. 205-206°. (Found : N, 10.9 ; Br, 26.6.  $C_{11}H_{13}O_2N_2Br$  requires N, 9.82 ; Br, 28.0 per cent).

Acetyl-4-bromo-*o*-anisylcarbamide, m.p. 232-34°. (Found : N, 9.18 ; Br, 28.7.  $C_{10}H_{12}O_3N_2Br$  requires N, 9.68 ; Br, 28.7 per cent).

Acetyl-1-bromo-*o*-phenetylcarbamide, m.p. 236-38°. (Found : N, 9.28 ; Br, 27.5.  $C_{11}H_{14}O_3N_2Br$  requires N, 9.30 ; Br, 26.6 per cent).

Acetyl-dibromo-*m*-phenetylcarbamide, m.p. 236-38°. (Found : N, 9.28 ; Br, 41.28.  $C_{11}H_{12}O_3N_2Br_2$  requires N, 7.36 ; Br, 42.1 per cent).

Bromoacetylurethane, m.p. 120-21°. (Found : N, 6.45 ; Br, 37.17.  $C_5H_8O_3NBr$  requires N, 6.65 ; Br, 38.09 per cent). In the case of this compound, no heating is required. Mere keeping overnight gives the product on evaporation of the solvent.

All these bromo compounds have also been synthesised from acetylurethane and the corresponding bromo-amino compounds and thus their constitution established.

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## ADDITION PRODUCTS OF ANILS WITH SOME METALLIC CHLORIDES

BY V. M. THAKOR AND R. C. SHAI

It is observed that ethyl acetoacetate and aniline when treated with fused zinc chloride give a crystalline addition product, ethyl acetoacetate-anil-zinc chloride, which is also obtained from ethyl acetoacetate-anil and zinc chloride. The addition product can be decomposed by sodium carbonate to get the anil. No such addition product of an anil is known in literature. Anil of ethyl  $\alpha$ -methylacetoacetate and *o*- and *p*-methyl- and *o*-methoxy-anils of ethyl acetoacetate gave similar crystalline addition products with zinc chloride. Similar addition products were also obtained from the above anils with cadmium and mercuric chlorides. Acetophenone-anil and benzaldehyde-anil did not give an addition product but got hydrolysed. This property of  $\beta$ -ketonic ester-anils can be used as a qualitative test for their detection or to separate them from a mixture or to obtain them in a pure form.

It is well known that ethyl acetoacetate reacts with aniline in two ways: Equimolecular proportions of both, when mixed and kept at room temperature, furnish the anil, with elimination of water (Conrad and Limpach, *Ber.*, 1887, **20**, 944, 948). On the other hand, if aniline is slowly added to ethyl acetoacetate at 160°, acetoacetanilide is formed, alcohol being eliminated (Knorr, *Ber.*, 1892, **25**, 772). The anil of ethyl acetoacetate at 280° furnishes 4-hydroxy-2-methylquinoline (Conrad and Limpach, *loc. cit.*); while the anilide on treatment with concentrated sulphuric acid gives 2-hydroxy-4-methylquinoline (Knorr, *Annalen*, 1888, **245**, 358, *et. seq.*).

In course of some synthetic work for preparing these hydroxyquinoline derivatives, fused zinc chloride was tried as a condensing agent for the reaction of aniline and ethyl acetoacetate. On working up, a well defined crystalline product was obtained which melted above 240° over a wide range and with decomposition. It decomposed on long exposure to air or in boiling water, smell of aniline being perceptible; with boiling alkali, aniline was formed. The usual qualitative tests showed the presence of zinc and halogen.

To determine the identity of the product aniline, ethyl acetoacetate-anil and acetoacetic anilide were separately treated with equimolecular amounts of zinc chloride. Aniline and the anil gave colorless addition products. The anilide was recovered unchanged. The addition product of aniline and zinc chloride differed considerably in properties from the above compound; while that from the anil resembled in all its properties to this compound. Thus, the substance under investigation appeared to be an addition product of the anil and zinc chloride. The results of analysis showed the presence of equimolecular proportions of the anil and zinc chloride. The substance, when treated with sodium carbonate, decomposed to give the anil which could be converted by Limpach's method (*Ber.*, 1931, **64**, 969) into 4-hydroxy-2-methylquinoline. Hence, the substance under investigation was an addition product of ethyl acetoacetate-anil and zinc chloride,  $\text{CH}_3\text{C}(\text{N}:\text{C}_6\text{H}_5)\text{CH}_2\text{COOC}_2\text{H}_5 \cdot \text{ZnCl}_2$ . Ethyl acetoacetate and aniline reacted in presence of fused zinc chloride to give the anil (cf. Reddelein, *Ber.*, 1909, **42**, 4759; 1910, **43**, 2476, 2480, *et. seq.*), which then formed an addition product with zinc chloride. No such addition product of an anil appears to be known in literature. The same addition product can be obtained in a pure state by mixing the anil and zinc chloride in rectified spirit solution.

Ethyl  $\alpha$ -methylacetoacetate-anil also gave an addition product with zinc chloride, which was also obtained from ethyl  $\alpha$ -methylacetoacetate, aniline and fused zinc chloride. On decomposition with sodium carbonate solution it gave the anil which could be converted into 4-hydroxy-2:3-dimethylquinoline. Various substituted anils, viz., *o*- and *p*-methyl- and *o*-methoxy-anils of ethyl acetoacetate gave similar crystalline addition products.

Similar addition products were also obtained from these anils with mercury and cadmium chlorides. Attempts were made to get such addition products from acetophenone-anil and benzaldehyde-anil. However, these anils got hydrolysed in presence of zinc chloride and aniline-zinc chloride was obtained.

Thus, the formation of additive products with the above metallic chlorides appears to be the property of anils of  $\beta$ -ketonic ester and can be used as a qualitative test for distinguishing these anils, or separating them from a mixture or getting them in a pure form.

## EXPERIMENTAL

*Addition Product of Ethyl Acetoacetate-anil and Zinc Chloride*

(1) Ethyl acetoacetate (4.3 g.), aniline (3.1 g.) and powdered fused zinc chloride (4.6 g.) were mixed. Considerable heat was evolved. It was heated on a steam-bath for two hours, water was added and the product washed thoroughly. It was crystallised from rectified spirit, in colorless prismatic needles (3.5 g.). It shrank at about 190° and melted in a range of 248°-255° with decomposition. (Found : Cl, 21.1.  $C_{12}H_{15}O_2N \cdot ZnCl_2$  requires Cl, 20.8 per cent).

(2) Ethyl acetoacetate-anil (Cavallito and Haskell, *J. Amer. Chem. Soc.*, 1944, **66**, 1166) (3.4 g.) and powdered zinc chloride (2.3 g.) were mixed and heated on a steam-bath for 2 hours. On working up, the above product of m.p. 239°-45° was obtained.

(3) The anil (3.4 g.) was dissolved in rectified spirit (7 c.c.) and a solution of zinc chloride in minimum amount of the same solvent added. Fine crystals of the product separated. The mixture was kept aside for some time and the crystals collected when the same product was obtained.

Ethyl acetoacetate-anil-zinc chloride has no sharp and definite melting point. It shrinks and appears to start melting at 190°, turns blackish at about 205° and actually melts between 230° and 260°. The melting point is found to vary in this range in different preparations. It starts decomposing at about 255°. On exposure to air the crystals slowly change colour to yellowish and then pinkish and there is a strong smell of aniline. It decomposes with hot water or dilute alkali giving aniline. Cold dilute hydrochloric acid has little effect. It is difficultly soluble in ethyl alcohol, acetone and acetic acid in cold, but dissolves quite readily on boiling. It is insoluble in other usual organic solvents.

*Decomposition of Ethyl Acetoacetate-anil-zinc Chloride with Sodium Carbonate*

The anil-zinc chloride (1 g.) was suspended in rectified spirit and sodium carbonate added, and the mixture well shaken when zinc carbonate precipitated. It was kept for about two hours, filtered and the filtrate extracted with ether. The extract was dried and ether removed. The oil that remained was found to be ethyl acetoacetate-anil as, (i) it did not dissolve easily in dilute hydrochloric acid, (ii) it gave the addition product with zinc chloride, and (iii) it could be converted into 4-hydroxy-2-methylquinoline, m.p. 230° by Conrad and Limpach's method (*loc. cit.* cf. Hughes and Louis, *J. Proc. Roy. Soc. N. S. Wales*, 1938, **71**, 458).

*Addition Product of Aniline and Zinc Chloride*

Aniline (3.1 g.) dissolved in rectified spirit was mixed with a solution of zinc chloride (2.3 g.) in the same solvent. Soon colorless plates of aniline-zinc chloride separated, m.p. above 220° with decomposition. (Found : Cl, 22.1.  $2C_6H_7N \cdot ZnCl_2$  requires Cl, 22.2 per cent). On exposure to air it turns pinkish giving a strong smell of aniline. It decomposes with hot water or dilute alkali. It is readily soluble in alcohol, acetone or acetic acid in cold, and insoluble in other usual organic solvents.

Several other addition products were prepared from various anils with zinc, cadmium and mercuric chlorides. The general method used was the same, namely, mixing equimolecular proportions of the two in rectified spirit solution when they separated as well defined crystals melting above 200° within a range and with decomposition, there being no sharp and definite melting point. In solubilities and other properties also they resemble ethyl acetoacetate-anil-zinc chloride. For the sake of brevity they are tabulated below.



TABLE I

No.	Anils.	Metallic chloride.	Product.	Shape of crystals.	M. p.	Chlorine	
						Found.	Calc.
1	Ethyl acetoacetate-anil	CdCl <sub>2</sub>	C <sub>12</sub> H <sub>15</sub> O <sub>2</sub> N, CdCl <sub>2</sub>	Colorless tiny needles	>220° (decomp.)	18.0%	18.3%
2	Do	HgCl <sub>2</sub>	C <sub>12</sub> H <sub>15</sub> O <sub>2</sub> N, HgCl <sub>2</sub>	Colorless columns	>120° (decomp.)	15.0	14.9
3	Ethyl $\alpha$ -methylacetoacetate-anil (a)	ZnCl <sub>2</sub>	C <sub>13</sub> H <sub>17</sub> O <sub>2</sub> N, ZnCl <sub>2</sub> (b)	Colorless prismatic needles	248-58° (decomp.)	19.8	20.0
4	Do	HgCl <sub>2</sub>	C <sub>13</sub> H <sub>17</sub> O <sub>2</sub> N, HgCl <sub>2</sub>	Colorless needles	145-75° (decomp.)	14.7	14.5
5	Ethyl acetoacetate-o-methylanil (c)	ZnCl <sub>2</sub>	C <sub>13</sub> H <sub>17</sub> O <sub>2</sub> N, ZnCl <sub>2</sub>	Slender needles	>230° (decomp.)	20.4	20.0
6	Do	CdCl <sub>2</sub>	C <sub>13</sub> H <sub>17</sub> O <sub>2</sub> N, CdCl <sub>2</sub>	Tiny silky needles	>220° (decomp.)	17.5	17.7
7	Ethyl acetoacetate-p-methylanil (c)	ZnCl <sub>2</sub>	C <sub>13</sub> H <sub>17</sub> O <sub>2</sub> N, ZnCl <sub>2</sub>	Tiny needles	>230° (decomp.)	20.1	20.0
8	Do	CdCl <sub>2</sub>	C <sub>13</sub> H <sub>17</sub> O <sub>2</sub> N, CdCl <sub>2</sub>	Fine needles	>220° (decomp.)	17.9	17.7
9	Ethyl acetacetate-o-methoxyanil (d)	ZnCl <sub>2</sub>	C <sub>13</sub> H <sub>17</sub> O <sub>3</sub> N, ZnCl <sub>2</sub>	Colorless needles	>220° (decomp.)	19.0	19.1
10	Do	CdCl <sub>2</sub>	C <sub>13</sub> H <sub>17</sub> O <sub>3</sub> N, CdCl <sub>2</sub>	Colorless tiny needles	>220° (decomp.)	17.2	17.0
11	Acetophenone-anil (e)	ZnCl <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> HN <sub>2</sub> , ZnCl <sub>2</sub> (f)	Colorless plates	>220° (decomp.)	—	—
12	Benzaldehyde-anil (g)	ZnCl <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> , ZnCl <sub>2</sub> (h)	Colorless plates	>220° (decomp.)	—	—

(a) Conrad and Limpach, *Ber.*, 1891, **24**, 2990.

(b) Also prepared from ethyl  $\alpha$ -methylacetoacetate, aniline and zinc chloride. On decomposition by sodium carbonate it gave back the anil which could be converted by Limpach's method into 4-hydroxy-2:3-dimethylquinoline (Wohnlich, *Arch. Pharm.*, 1913, **251**, 535).

(c) Conrad and Limpach, *Ber.*, 1888, **21**, 523.

(d) *Idem*, *ibid.*, p. 1649.

(e) Reddelein, *ibid.*, 1910, **43**, 2478.

(f) A strong smell of acetophenone developed when the reactants were mixed. The product on decomposition gave only aniline (isolated as hydrochloride, m.p. 196-97°), no acetophenone being isolated.

(g) Organic Synthesis, Col. Vol. I, p. 80.

(h) A strong smell of benzaldehyde developed in the mixture. The product on decomposition gave only aniline (hydrochloride, m.p. 198°), no benzaldehyde could be isolated.

### ON ORGANO-ARSENICAL COMPOUNDS. PART III

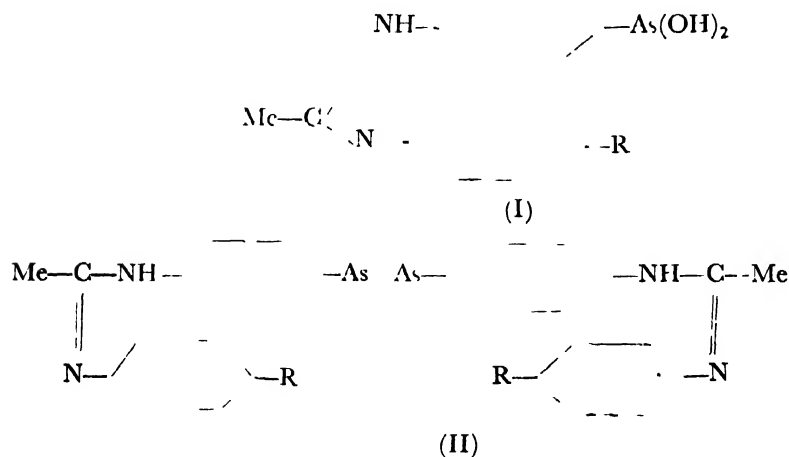
By B. PATHAK AND T. N. GHOSH

Some N-alkylated amidines containing the arsenious acid group have now been synthesised by reacting aceto-*p*-phenetidine or a otanilide with *p*-arsanilic acid in presence of  $\text{PCl}_3$  or  $\text{POCl}_3$ .

In view of the promising results in the chemotherapy of filariasis, as obtained with some arsenoxide derivatives by Otto and Maen (*Science*, 1947, **106**, 105), and in view of the pronounced parasitocidal property of various amidine derivatives (King, Lourie and Yorke, *Lancet*, 1937, **233**, 136 ; Kirk and Sati, *Ann. Trop. Med. Parasitol.*, 1940, **34**, 82) it has been considered desirable to synthesise some amidine derivatives containing arsenoxide group, so that these compounds may be tested for any filaricidal activity.

Hofmann (*Jahresber. Fort. Chem.*, 1865, 114; *Monatsberichte Berl. Akad.*, 1865, p.640) obtained diphenylacetamidine and diphenylbenzamidine by condensing aniline with acetanilide and benzanilide respectively, in presence of  $\text{PCl}_3$  or  $\text{PCl}_5$ . This method is of general applicability and has been utilised by subsequent workers (Bamberger and Lorenzen, *Annalen*, 1893, **273**, 269 ; Hill and Robinowitz, *J. Amer. Chem. Soc.*, 1926, **48**, 732 ; Sen and Ray, *J. Chem. Soc.*, 1926, 646) for the synthesis of a number of new N-alkylated amidines.  $\text{PCl}_3$  is the most suitable condensing agent for the above reaction, although  $\text{P}_2\text{O}_5$  (Schuler, U. S. patent, 1,384, 637) or  $\text{POCl}_3$  (Bures and Kundera, *Časopis Českoslov. Lékařstva*, 1934, **14**, 272) may also be used sometimes with advantage.

By condensing aceto-*p*-phenetidine with *p*-arsanilic acid in presence of  $\text{PCl}_3$ , the compound (I,  $\text{R}=\text{OEt}$ ), which is an acetamidine derivative containing the arsenious acid group, has now been obtained. The isolation of the arsenious acid derivative, instead of the corresponding arsonic acid, is ascribed to the fact that  $\text{PCl}_3$  very easily reduces arsonic acids to arsenoxides (cf. Ehrlich and Bertheim, *Ber.*, 1910, **43**, 920 ; Karrer, *Ber.*, 1914, **47**, 2275). By further reducing the compound (I,  $\text{R}=\text{OEt}$ ) with hypophosphorus acid in presence of a trace of potassium iodide, the corresponding arseno derivative (II,  $\text{R}=\text{OEt}$ ) has now been obtained.



The above compound (I,  $\text{R}=\text{OEt}$ ) and an arsenic-free compound (which could not be characterised due to its poor yield) have been obtained, when the above reaction was carried out in presence of  $\text{POCl}_3$ , instead of  $\text{PCl}_3$ . In this connection reference is made to the reduction

of 2-chlorovinylarsonic acid to 2-chlorovinylchloroarsine by  $\text{POCl}_3$  (Hewett, *J. Chem. Soc.*, 1948, 1204). The compound (I,  $\text{R}=\text{OEt}$ ) readily decolorises iodine solution and remains unaffected when treated with sulphur dioxide in presence of potassium iodide. Moreover, in conformity with the characteristic property of arsenoxides, it dissolves in dilute caustic soda (though insoluble in aqueous bicarbonate or ammonia) solution, from which the free arsenious acid is salted out by saturating with sodium chloride. That the compound (I,  $\text{R}=\text{OEt}$ ) is an arsenious acid and not an arsonic acid derivative has been further confirmed by reacting *p*-aminophenylarsenoxide (Ehrlich and Berthelm, *Ber.*, 1910, 43, 917) with aceto-*p*-phenetidine in presence of  $\text{POCl}_3$ , when a compound identical with (I,  $\text{R}=\text{OEt}$ ) has been obtained.

Similarly, by reacting acetanilide with *p*-arsanilic acid in presence of  $\text{POCl}_3$ , a mixture of the compound (I,  $\text{R}=\text{H}$ ) and 4-anilinoquinaldine (Conrad and Limpach, *Ber.*, 1887, 20, 953; Backeberg, *J. Chem. Soc.*, 1931, 2814) has been obtained. The compound (I,  $\text{R}=\text{H}$ ) which gives all the characteristic tests of arsenious acid, as described above, has been further reduced by hypophosphorus acid in presence of potassium iodide to the arseno derivative (II,  $\text{R}=\text{H}$ ).

## EXPERIMENTAL

### (Phenyl-4-ethoxy)-(phenyl-4-arsenious acid)-acetamidine (I, $\text{R}=\text{OEt}$ )

(a). An intimate mixture of aceto-*p*-phenetidine (9 g.) and *p*-arsanilic acid (11 g.) was gradually added to phosphorus trichloride (60 c.c.). Heat developed and the mixture was heated in an oil-bath at 100°-105° for about 4 hours. Next day, the reaction mixture was poured into crushed ice, when a pasty mass was obtained. The supernatant liquid was decanted, filtered and treated with excess of ammonium hydroxide, when a solid was precipitated, which was filtered. It is soluble in alcohol and acetic acid, and sparingly in hot water, and it could not be crystallised from any of these solvents. It was therefore purified by washing with ammonium hydroxide and then trituration with 10% caustic soda solution. The alkaline solution, after treatment with charcoal, was just neutralised with hydrochloric acid, when a colorless solid (4 g.) was obtained, which shrank at 100° and melted to a brown viscous mass at 134-35°. (Found: N, 7.42; As, 19.85.  $\text{C}_{16}\text{H}_{19}\text{O}_3\text{N}_2\text{As}$  requires N, 7.73; As, 20.70 per cent). It is readily soluble in dilute hydrochloric acid and in dilute alkali but insoluble in aqueous ammonia or bicarbonate. Its acetic acid solution readily decolorises iodine solution and it remains unaffected when its solution in dilute sulphuric acid is saturated with sulphur dioxide in presence of a trace of potassium iodide. From its solution in 10% caustic soda solution it is precipitated as such when saturated with sodium chloride.

From the pasty mass, described above, a further quantity (1 g.) of the compound (I,  $\text{R}=\text{OEt}$ ) was obtained by trituration with 10% caustic soda solution, filtration and careful neutralisation with just the requisite quantity of hydrochloric acid. It was subsequently purified as above.

(b). The above reaction was carried out with the same quantities of the reactants in phosphorus oxychloride (60 c.c.) at 125°-130° for about 4 hours. Next day, the reaction mixture was poured into crushed ice, when a pasty mass was obtained. The supernatant liquid was decanted and, when treated with excess of ammonium hydroxide, yielded a tarry mass which could not be purified. The pasty mass was washed with water and then thoroughly trituated with excess of cold caustic soda solution (10%). The major portion went into solution and the insoluble solid was filtered. The alkaline solution was just neutralised with hydrochloric acid when a solid (3 g.) was obtained. It was purified as above, and found identical with the compound (I,  $\text{R}=\text{OEt}$ ) by a study of its properties and also by analysis.

The alkali-insoluble solid was first purified by solution in dilute hydrochloric acid and precipitation with dilute alkali, and it was finally crystallised from alcohol in colorless needles, m.p. 122-24°. It contains chlorine and no arsenic and its extremely poor yield precluded further study and characterisation.

(c). The condensation of *p*-aminophenylarsenoxide with aceto-*p*-phenetidine in presence of phosphorus oxychloride has been studied under the same experimental conditions as described

above. The method of isolation of the reaction products was the same as above. Besides an arsenic-free compound (m.p. 122-24°) which contains chlorine, a compound, proved to be identical with (I, R=OEt) by a comparative study of their properties and by analysis, has been obtained.

(4:4'-Diethoxydiphenyl)-(4:4'-arsenophenyl)acetamidine (II, R=OEt).—The compound (I, R=OEt; 4 g.) in 150 c.c. of water and 8 c.c. of concentrated hydrochloric acid, was reduced by adding, with stirring, 35% hypophosphorus acid (25 g.) and 2 c.c. of 1% aqueous solution of potassium iodide. Soon a precipitate came out and the reaction mixture was stirred at room temperature for about 2 hours. The solid was filtered, washed thoroughly with water and dissolved in acetic acid. The acetic acid solution was then basified, under cooling, with caustic soda solution, when a cream-coloured solid (2g.) was obtained, which was filtered and washed thoroughly with water. It melts at 178-80° to a brown, viscous mass; it is insoluble in dilute alkali. (Found: As, 22.18.  $C_{32}H_{34}O_2N_4As_2$  requires As, 22.83 per cent).

(Phenyl)-(phenyl-4-arsenious acid)-acetamidine (I, R=H).—An intimate mixture of acetanilide (14 g.) and *p*-arsanilic acid (22 g.) was added to phosphorus oxychloride (100 c.c.), and the solution was heated under reflux at 120° for about 4 hours.

From the reaction mixture two compounds, of which one is insoluble in alkali and the other is soluble, have been isolated. The former was purified by solution in acetic acid and precipitation by excess of ammonium hydroxide. It was crystallised from alcohol in colorless needles (5.8 g.), melting at 155-56° and was found to be identical with an authentic sample of 4-anilinoquinaldine (Backeberg, *loc. cit.*).

The alkali-soluble compound (I, R=H) was purified as described previously and was obtained as a colorless solid (6g.) which was dried at 60°-65° *in vacuo*. It melts at 146-48° to a viscous mass. (Found: N, 8.45; As, 22.97.  $C_{14}H_{15}O_2N_2As$  requires N, 8.80; As, 23.57 per cent).

(Diphenyl)-(4:4'-arsenophenyl)-acetamidine (II, R=H).—The method of preparation was the same as in the case of the compound (II, R=OEt). The cream-coloured solid melts at 168-70° to a brown, viscous mass and is insoluble in alkali. (Found: As, 24.05.  $C_{30}H_{30}ON_4As_2$  requires As, 24.49 per cent).

## INTERACTION OF SULPHUR DIOXIDE AND HYDROGEN UNDER SILENT ELECTRICAL DISCHARGE

By G. S. DESHMUKH AND B. LAHIRY

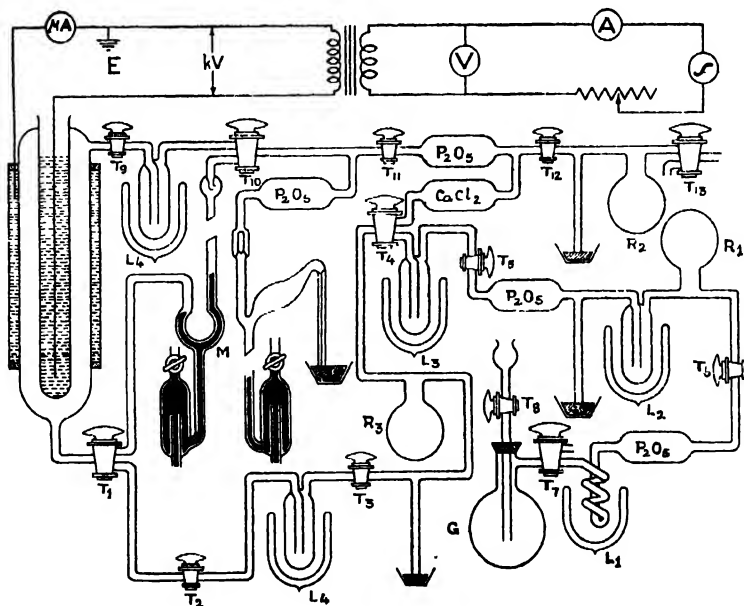
Interaction of  $\text{SO}_2$  and  $\text{H}_2$  under silent electric discharge is time-continuous and irreversible. An initial rapid fall of the pressure ( $p$ ) is followed by a slower change and the attainment of a stationary stage. The time variation of the conductivity,  $i$ , is synchronous with but less pronounced than that of  $p$ . The formation of  $\text{SO}$  as an unstable intermediate product is suggested. Besides  $\text{H}_2$  and undecomposed  $\text{SO}_2$ , the reaction products consist of sulphur,  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{SO}_3$ ,  $\text{O}_2$ ,  $\text{O}_3$  and  $\text{H}_2\text{S}$ . Ozone is produced prior to  $\text{H}_2\text{S}$ . The decrease of  $p$  is attributed to the condensation of the products of decomposition or/and their 'clean up' by the annular film of sulphur produced under the discharge. In agreement with the general finding due to Joshi the current  $i$ , at a given applied potential  $V$ , depends on  $V - V_m$ , where  $V_m$  is the 'threshold potential'. Production of  $\text{SO}$  and  $\text{SO}_3$  reduces  $V_m$  and tends to increase  $i$ . The deposition of sulphur on the annular walls inhibits the reaction.

During the reaction between nitrous oxide and hydrogen, subjected to a silent discharge, observation was made of a remarkable 'periodic effect' in which the gas pressure, the current  $i$ , wattage dissipated in the system, as also the nature of the glow showed marked and synchronous discontinuities repeated over as long as 20 hours of exposure (Joshi, *Proc. Indian Sci. Cong.*, 1943, Part II, pp. 70-75; Joshi and Deshmukh, *Nature*, 1945, **155**, 483). According to Joshi (*Curr. Sci.*, 1946, **15**, 281) 'wall effect', formation of condensed products, and a spontaneous reaction reversal (despite constancy of exciting conditions,) constitute *inter alia* chief determinants of the 'periodic effect'. A reaction reversal was also observed in the interaction of sulphur and nitrogen (Deshmukh and Sirsakar, *Proc. Ind. Acad. Sci.*, 1948, **28A**, 175). Present work was undertaken since condensed products appeared likely in the reduction under discharge of  $\text{SO}_2$  which might produce the periodic phenomenon mentioned above.

### EXPERIMENTAL

The general arrangement of the apparatus and the electrical circuit employed are shown in Fig. 1. This consists of a generator  $G$  for preparing  $\text{SO}_2$ , the reservoirs  $R_1$ ,  $R_2$  and  $R_3$  to

FIG. 1



store  $\text{SO}_2$ ,  $\text{H}_2$  and their mixture respectively, liquid air traps  $\text{L}_1$ - $\text{L}_5$  for freezing out  $\text{SO}_2$  and other condensible products of decomposition, a Siemens' type glass ozoniser, a Töpler pump to evacuate any or all parts of the apparatus, a manometer  $\text{M}$  to record the pressure of the gaseous mixture in the ozoniser and drying tubes containing phosphorus pentoxide and calcium chloride.

The entire assembly was tested initially for vacuum for at least 48 hours. Sulphur dioxide was prepared in  $\text{G}$  by the action of sulphuric acid on sodium bisulphite. The gas was purified by fractionation over liquid air in  $\text{L}_1$  and the middle fraction was stored in  $\text{R}_1$ . Hydrogen was obtained from a commercial cylinder. The gas was bubbled slowly through traps filled with a freshly prepared solution of alkaline pyrogallol. It was dried carefully over  $\text{P}_2\text{O}_5$  and  $\text{CaCl}_2$  and was finally admitted through the tap  $\text{T}_{13}$  to the reservoir  $\text{R}_2$ . The gaseous mixture was prepared by solidifying  $\text{SO}_2$  in  $\text{L}_3$  cooled by liquid air.  $\text{T}_5$  was now closed. Hydrogen was introduced in  $\text{R}_3$  through  $\text{T}_{12}$  and  $\text{T}_4$ .  $\text{R}_3$  was then connected with  $\text{L}_3$  by proper manipulation of  $\text{T}_4$ . The liquid air bath was removed carefully and sulphur dioxide allowed to vaporise. Results now reported refer to two stock mixtures: (1) consisting of 32%  $\text{H}_2$  and 68%  $\text{SO}_2$  and (2) containing 83%  $\text{H}_2$  and 17%  $\text{SO}_2$ .

Single phase alternating current of 50 cycles frequency obtained from a rotary converter worked off 220 volt D.C. supply was fed to the primary of a 3 KVA transformer. One of its secondaries was earthed; the other was dipped in a moderately concentrated salt solution forming the H. T. terminal of the ozoniser. The outer electrode was earthed through an oxide rectifier type A. C. milliammeter (MA in Fig. 1). The applied potential expressed in kilovolts (r.m.s.) kV, was calculated from a knowledge of the step-up ratio of the transformer and the primary potential  $V$ .

The gaseous mixture was introduced in the ozoniser at a desired pressure through  $\text{T}_3$ ,  $\text{T}_2$  and  $\text{T}_1$ . The system was excited at a given (fixed) applied potential  $V$ . The progress of the reaction was followed by the observation of the variation of the gas pressure  $p$ , the discharge current  $i$  and the nature of the glow. Two typical sets of observations are recorded in Tables I and II. Fig. 2 shows the time variation of  $p$  and  $i$  at 6.7 kV and an initial pressure of 10.5 cm. Hg of the first stock mixture. The products of decomposition were analysed at (a) a constant pressure and (b) the maximum current stage. At the end of a given exposure to discharge the decomposition mixture was led through the trap  $\text{L}_4$ , immersed in liquid air. The uncondensable products were collected over mercury in a gas burette by working the Töpler and were analysed for hydrogen and oxygen. The liquid air bath was removed and the condensable products allowed to vaporise. These were collected in another gas burette and tested for  $\text{SO}_2$ . The ozoniser was washed thoroughly with distilled water. This was also analysed (qualitatively) for the presence of  $\text{H}_2\text{SO}_3$  and  $\text{H}_2\text{SO}_4$ . The results of analysis (by volume at N. T. P.) are shown in Table III.

TABLE I

Applied potential=6.7 kV (r.m.s.) ; 50 cycles sec.  $^{-1}$   
Mixture No. 1 ( $\text{H}_2/\text{SO}_2$  = 32/68) : 18.5°

Time (min.)	0	5	10	15	20	25	30	35	40	45	50	60	70	80	90	100	110	150
Pressure (cm. Hg)	19.9	17.6	16.2	15.5	14.2	13.2	12.4	11.3	10.4	9.6	9.0	7.8	7.0	6.3	5.9	5.6	5.4	4.9
Current (mA)	0.1	0.11	0.13	0.12	0.14	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.15	0.13	0.13	0.12	0.12	0.12
Remarks	Manometric Hg. fouled. White deposit in the ozoniser.						Liquid droplets observed on the annular surface.				White deposit disappears in patches.				Liquid deposit disappears leaving a yellowish solid residue.			

TABLE II

Applied potential=6.7 kV (r.m.s.) ; 50 cycles sec. <sup>-1</sup>Mixture No. 2 (H<sub>2</sub>/SO<sub>2</sub>=32/68) ; 21°.

An ozone trap is connected with the ozoniser.

Time (min.)	0	5	10	15	30	45	90	135	165	195	210	240	300	Discontinue.
Pressure (cm. Hg.)	2.4	1.7	1.2	0.9	0.5	0.45	0.4	0.3	0.3	0.3	0.3	0.3	0.3	Found the black deposit on Hg to be HgS.
Current (mA)	0.29	0.26	0.26	0.26	0.22	0.22	0.24	0.24	0.23	0.24	0.21	0.24	0.24	
Remarks	Manometric Hg. fouled.						Blackening of the capillary leading to the ozone trap.				A black speck appeared on the surface of Hg in ozone trap.			

TABLE III

Mixture No.	Initial press. (cm. H <sub>2</sub> )	Applied kV.	Duration of discharge (min.)	Stage of analysis.	Total vol. of gas collected at N.T.P.	Vol. of SO <sub>2</sub> at N.T.P.	Vol. of H <sub>2</sub> at N.T.P.	Vol. of O <sub>2</sub> at N.T.P.	%SO <sub>2</sub> .	%H <sub>2</sub> .	%O <sub>2</sub> .
1. (H <sub>2</sub> /SO <sub>2</sub> = 32/68)	10.4	6.7	185	Const. press.	3.4 c.c.	1.88 c.c.	1.40 c.c.	0.12 c.c.	55.3	41.1	3.5
	10.2	6.7	41	Max. current	5.0	2.88	1.95	0.17	57.6	39.0	3.4
2. (H <sub>2</sub> /SO <sub>2</sub> = 83/17)	10.5	6.7	90	Const. press.	3.93	0.54	3.30	0.1	13.6	84.1	2.3
	10.4	6.7	28	Max. current	4.0	0.71	3.2	0.1	17.8	80.0	2.2

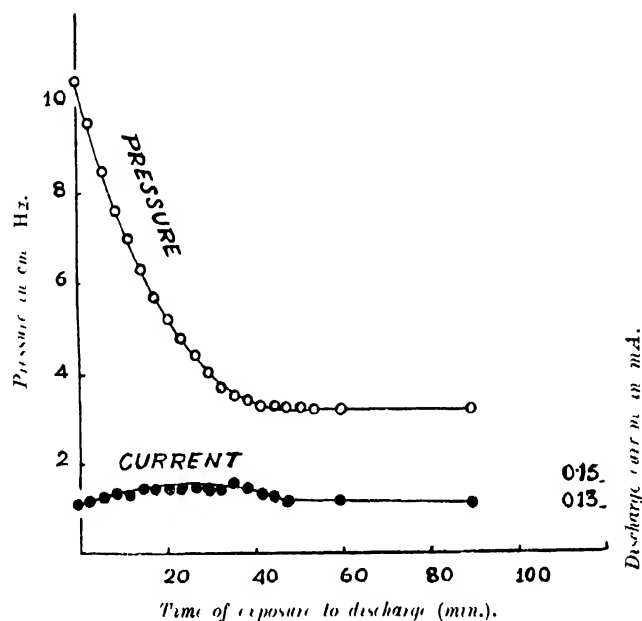
## DISCUSSION

Results in Fig. 2 and Tables I and II indicate that the interaction of SO<sub>2</sub> and H<sub>2</sub> under electrical discharge is time-continuous and irreversible. The pressure-time curve in Fig. 2 (which is but typical of a series of results) shows an initial rapid fall, followed by slower change and the attainment of a stationary minimum stage. Thus *e.g.* at 6.7 kV pressure decreased from 10.5 to 4.0 cm. Hg. *i.e.* by 62% in 30 minutes and from 4.0 to 3.2 cm. *i.e.* by about 20% in 24 minutes of exposure to discharge. *p* remained sensibly constant at this stage even after prolonged exposure to discharge for about 100 minutes. The discharge current *i* flowing through the reaction vessel varied synchronously with *p* though not in the same sense. *i* increased initially from 0.135 to 0.15 mA *i.e.* by 11% in 15 minutes, remained stationary for the next 24 minutes and decreased again to the initial minimum of 0.135 mA in 9 minutes of exposure to discharge. The attainment

of the constant stage was more or less simultaneous in both the pressure—time and current—time curves (cf. Fig. 2).

FIG. 2

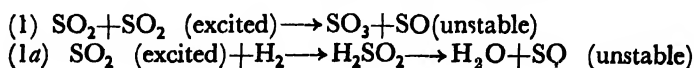
*Pressure-current variation during  $\text{SO}_2$ - $\text{H}_2$  interaction at 6.7kv; 50 cycles sec.<sup>-1</sup>*



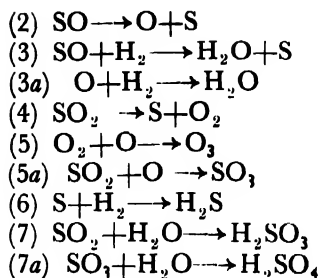
During experiments to which Table I refers, the formation of liquid droplets was observed on the annular walls of the ozoniser. It was interesting to note that the conductivity also increased to its maximum value during this stage of the reaction. The liquid product disappeared slowly leaving behind a yellowish solid residue when the current, as also the pressure of the reaction mixture, tended to reach the stationary minimum. Amongst the reactions products (besides  $\text{H}_2$  and undecomposed  $\text{SO}_2$ ) sulphur,  $\text{H}_2\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  were detected by the usual chemical tests. The fouling of the manometric mercury during the course of the reaction indicated the presence of ozone or/and  $\text{H}_2\text{S}$ . Series of experiments (of which the results given in Table II are but typical) were therefore next made by connecting an ozone trap (not shown in Fig. 1) between the ozoniser and the tap  $T_1$ . In all these cases the detection of  $\text{HgO}$  and  $\text{HgS}$  during successive stages of the reaction showed that the formation of  $\text{H}_2\text{S}$  was preceded by that of ozone.

Data for the analysis of the products of the reaction at the constant pressure and maximum current stage for the two stock mixtures containing different proportions of  $\text{SO}_2$  and  $\text{H}_2$  are recorded in Table III. The results are similar except that the amounts of the gaseous products of decomposition are different due to the varying proportions of  $\text{SO}_2$  and  $\text{H}_2$  in the stock mixtures.

The foregoing results suggest that the following reactions constitute the overall mechanism of the interaction of  $\text{SO}_2$  and  $\text{H}_2$  under silent discharge :







Starting from the primary reaction (1) all the subsequent steps follow. The production of SO has been postulated by many investigators (Cordes and Schenk, *Z. Electrochem.*, 1933, **39**, 594). Harteck and Gieb (*Ber.*, 1933, **66**, 1815; *Z. physikal. Chem.*, 1934, **170**, 1; *Trans. Faraday Soc.*, 1934, **30**, 131) advanced evidence from spectroscopic and thermochemical data for the formation of SO by the decomposition of an intermediate product  $\text{H}_2\text{SO}_2$ . (1) and (1a) are therefore suggested for the initial stage in the interaction of sulphur dioxide and hydrogen. With the exception of (6) all the reactions mentioned above may lead to the observed decrease of pressure due to the formation of condensible or/and adsorbable products of reaction such as  $\text{SO}_3$ ,  $\text{H}_2\text{O}$  and S. The reduction of  $p$  may also be due to the 'clean up' of hydrogen (Newman, *Trans. Amer. Electrochem. Soc.*, 1924, **44**, 77) and other gaseous products by the annular deposit of sulphur produced in (2), (3) and (4). Repeated observations have shown that  $\text{H}_2\text{S}$  occurs only during the last stage of the reaction. The step  $\text{SO} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + \text{O}$  is therefore not considered along with (3). The production of  $\text{H}_2\text{S}$  according to this reaction at a later stage is also considered unlikely in view of the instability of SO formed during the initial stage. According to Thomson and Hinselwood (*Proc. Roy. Soc.*, 1929, **A**, **122**, 616) the presence of sulphur dioxide does not affect the  $\text{H}_2 - \text{O}_2$  reaction. The production of  $\text{H}_2\text{O}$  according to (3a) is therefore suggested. Joshi and Sharma (*J. chim. phys.*, 1934, **31**, 511) studied the decomposition of sulphur dioxide under silent electrical discharge. The decomposition mixture contained SO,  $\text{O}_2$ , about 10% undecomposed  $\text{SO}_2$  and two unidentified solid products. 'SO decomposes under electrical discharge to produce S and  $\text{SO}_3$  and the free sulphur combines with  $\text{SO}_3$  to give a viscous liquid which absorbed  $\text{SO}_2$ ' (Berthelot, *Ann. chim. phys.*, 1898, *vii*, **14**, 167). The occurrence of the liquid product as observed may therefore be ascribed to the condensation of  $\text{SO}_3$  or/and the formation of absorption complexes of S,  $\text{SO}_2$  and  $\text{SO}_3$  on the walls of the ozoniser. The slow diminution of pressure, indicative of the retardation of the reaction, may be due, in part, to deposition of sulphur on the annular walls. The production of ozone in presence of a large proportion of hydrogen is remarkable. This agrees with the results obtained in the  $\text{N}_2\text{O} - \text{H}_2$  reaction under silent discharge where ozone and a series of higher oxides of nitrogen were detected despite the presence of excess of hydrogen (Joshi and Deshmukh, *loc. cit.*).

According to Joshi (*Trans. Faraday Soc.*, 1929, **25**, 118, 137; *Curr. Sci.*, 1939, **8**, 548) the discharge current  $i$  depends on  $V - V_m$ . Since  $i$  increases with the appearance of the liquid products (obtained presumably due to condensation of  $\text{SO}_3$ ), it may be assumed that its production lowers the 'threshold potential'  $V_m$ . A simultaneous decrease of  $i$  and also the corresponding reaction rate, as judged by the time variation of  $p$ , may be associated with the deposition of sulphur or/and the formation of adsorption complexes on the walls of the ozoniser.

Grateful thanks of the authors are due to Prof. S. S. Joshi for suggesting the problem and kind guidance during the work.



*Born of experience*



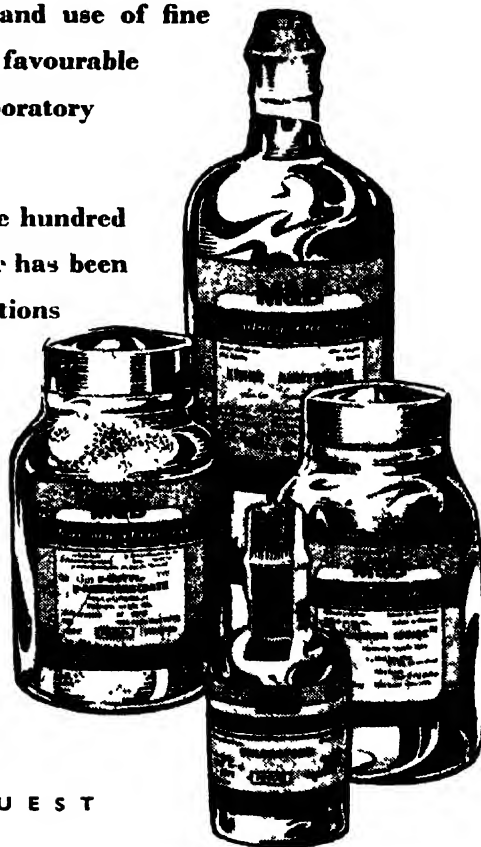
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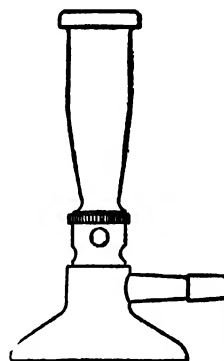
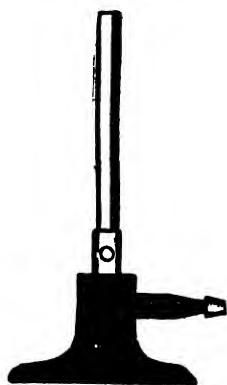
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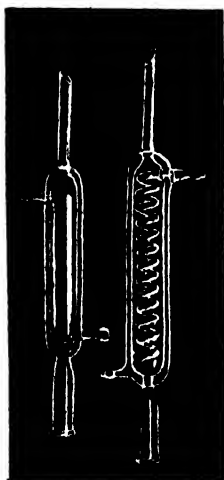
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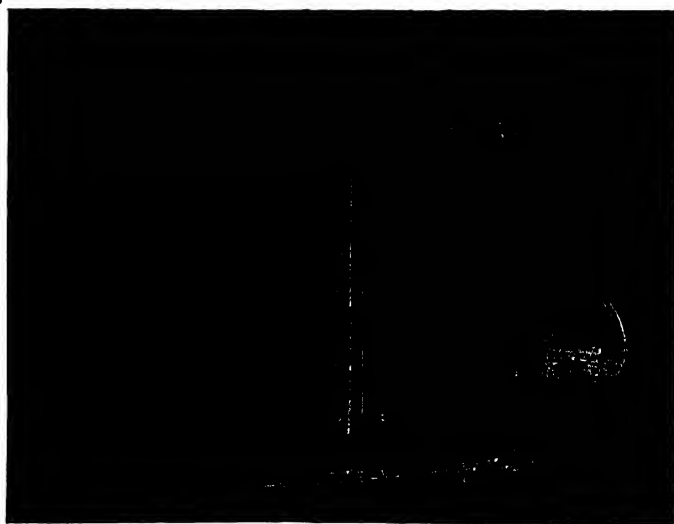
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## ADSORPTION OF VAPOURS ON SILICA GEL AT LOW PRESSURES

BY B. P. GYANI

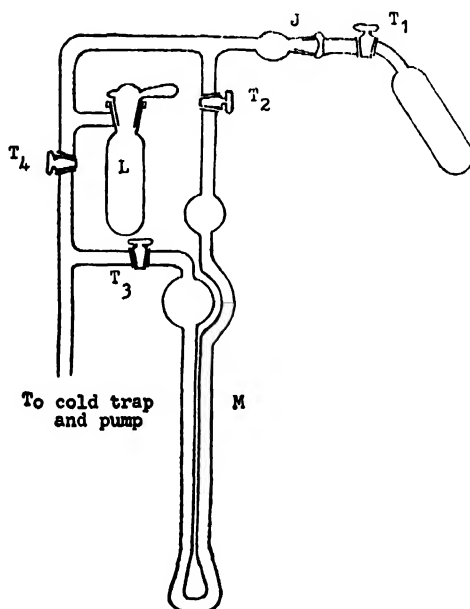
Adsorption of ethyl alcohol and carbon tetrachloride at 25° on silica gel has been measured at reduced pressures with the help of a sensitive manometer. It has been found that the whole of the carbon tetrachloride in the adsorbed state may be confined to a two dimensional space which is not true for the adsorption of alcohol. The form of the Langmuir adsorption isotherm at low pressures has been considered and it is found that the Henry's law need not necessarily apply in these circumstances.

Measurements of adsorption in the pressure range of 0.1 to a few mm. of mercury are few in existence. The mercury manometer is not sufficiently sensitive to explore the adsorption in this region and conditions do not exist for the satisfactory working of such sensitive devices as the Pirani gauge or the viscosity gauges. In working with vapours little reliance can be put in the McLeod gauge. Though the experimental difficulties are considerable this region is of importance in understanding the nature of adsorption. For, secondary factors that set in due to increase of pressure are mainly absent so that the different equations of adsorption can be put to a more rigorous test than usual. It was with these intentions that the following measurements were undertaken.

### EXPERIMENTAL

The apparatus used for these experiments is shown in Fig. 1. The mercury manometer used in previous measurements (*J. Phys. Chem.*, 1945, **49**, 226) was replaced by one of oil

Fig. 1



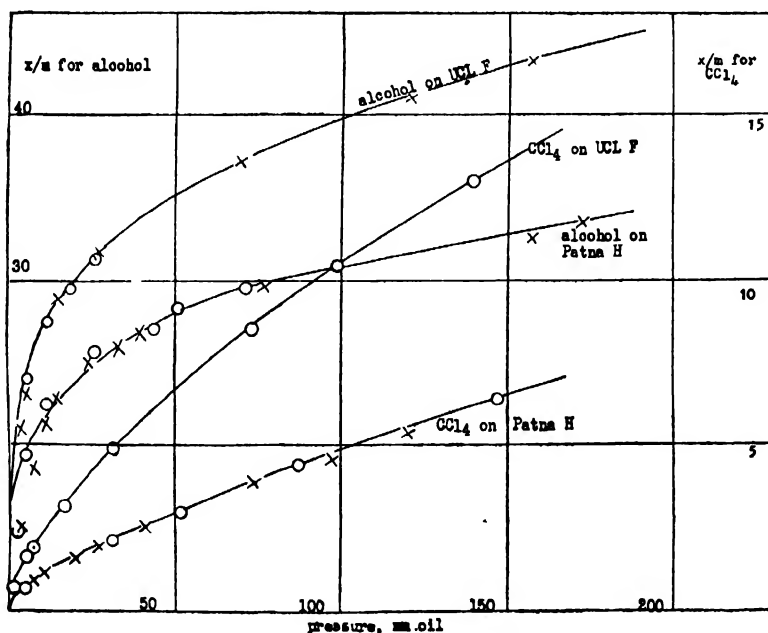
(M) and was so arranged as to eliminate zero error. A liquid trap, cooled in solid carbon dioxide, was interposed between the apparatus and the pump. It prevented effectively

any vapour from reaching the latter. To measure the pressure inside the apparatus the pump was started and  $T_3$  gradually opened, followed by  $T_2$ . The zero error was thus kept down to the efficiency of the pump which was better than  $10^{-3}$  mm. The difference in level on the two sides could be read directly on a scale rigidly attached to the manometer as usual with a telescope. An Apiezon oil of low density and moderate viscosity was chosen for use in the manometer. The density being 0.872, 1 mm. of oil = 0.0644 mm. of Hg or 1 mm. of mercury = 15.52 mm. of oil

The oil in the manometer was freed from dissolved air by pumping hard while the liquid was cautiously heated. The bulbs on M were meant for catching the copious froth produced. The vapours were swept out from the manometer after each measurement, the taps  $T_2$ ,  $T_3$  being kept usually closed. One has to be careful in manipulating the taps, for a slight pressure difference between the two limbs may throw the oil violently on one side and thence into the main apparatus. It is also necessary to employ tubings of at least 4 mm. bore in constructing the manometer to prevent the oil column from breaking at times.

Two samples of silica gel described previously (Thesis, London, 1947, p. 25) have been used. One sample, UCL F, prepared at the University College, London, was about three months old and had been evacuated for 2 hours at  $300^\circ$ - $320^\circ$ . The other sample, Patna H, prepared at Patna, was three years old and had been evacuated at the same temperature. Uniform electrical heating was employed in each case. The gel was flushed several times with vapour before commencement of the first run. The whole apparatus was maintained at  $25^\circ$  throughout these measurements.

Fig. 2



The results of these measurements are shown graphically in Figs. 2, 3 and 4. Fig. 2 shows the plot of the amount of adsorption per unit weight of the gel,  $x/m$ , expressed in g. mol. of

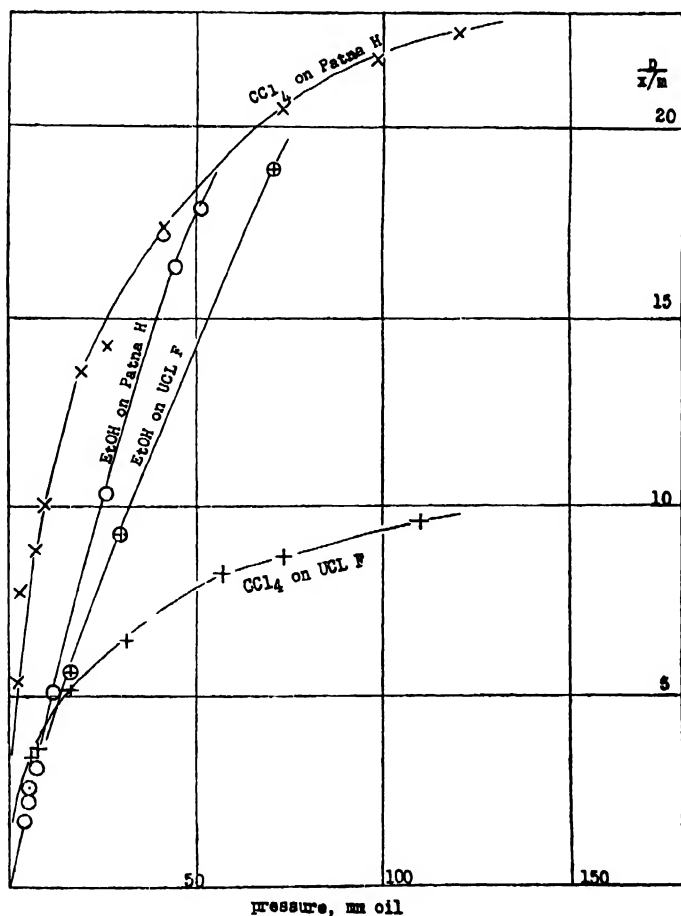


the liquid  $\times 10^4$ , against pressure  $p$  in mm. of oil. The forms of the isotherms are the same as obtained earlier with a mercury manometer in the same pressure range. Also, the amounts of adsorption at corresponding pressures in the two sets of data are substantially the same (Gyani, Thesis, London, 1947, p.19 and Fig. 11). Saturation has not set in yet in the range of these pressures.

### DISCUSSION

The low pressure measurements with alcohol establish the existence of the initial, almost vertical rise of the  $x/m$ - $p$  isotherm at pressures too small to measure (McBain, "Sorption of Gases and Vapours", p.128 *et seq.*, London, 1932). The upper limit of this pressure could not be larger than 0.006 mm. of mercury, since such a pressure could no doubt have been detected if not measured on the oil manometer. It is also proved with certainty that no appreciable quantity of carbon tetrachloride is retained by either gel at low pressures. Fig. 2

Fig. 3

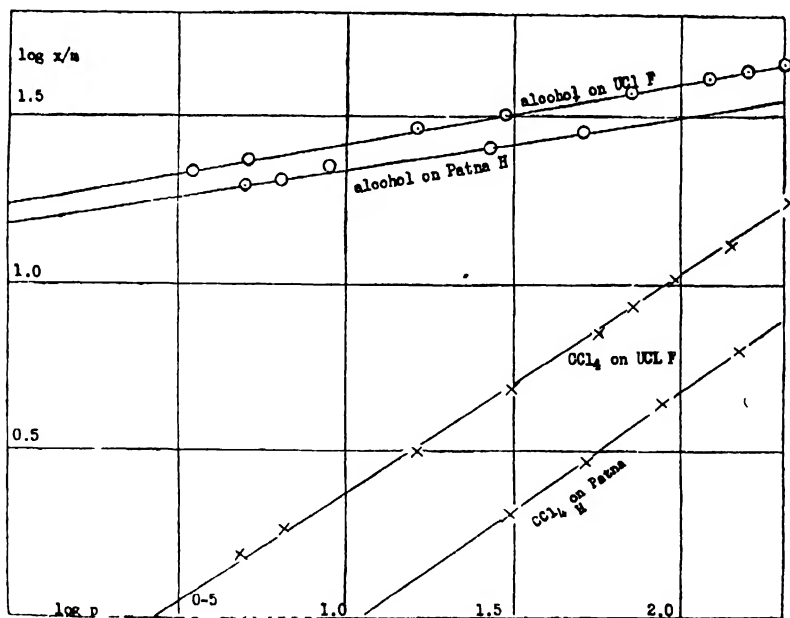


shows that the plot of  $x/m$  against  $p$  does not approximate to a straight line even when one confines oneself to pressures as low as 50 mm. of oil which corresponds to only 3 mm. of mer-

cury, but this fact as commonly supposed is not against the applicability of the Langmuir adsorption equation as shown below.

Fig. 3 shows the plot of  $\frac{p}{x/m}$  against  $p$  for both the compounds. The curves have a curvature concave towards the pressure side which is only slight in the case of alcohol but strong in the case of carbon tetrachloride. The data are therefore not in agreement with the Langmuir equation. To test the present data for a fit with the classical adsorption equation,  $\log x/m$  has been plotted against  $\log p$  for both the compounds in Fig. 4. The alcohol isotherm has a smaller slope than the one for carbon tetrachloride, but each is a satisfactory straight line in the range of these measurements. One may conclude that the classical equation fits the data much more satisfactorily than the Langmuir equation. It may be of interest to point out that separate experiments have shown that the heat of adsorption of carbon tetrachloride on silica gel is particularly variable with the amount of adsorption (Gyani, Thesis, London, 1947, p.103). The heat of adsorption fell from 9344 cal. per mol. of the liquid to 8782 as the amount of adsorption was decreased from  $50.10 \times 10^{-4}$  g. mol. per g. of the gel to 35.80. This variation is not recognised in the simple deduction of the Langmuir equation.

Fig. 4



Another point of interest in these measurements concerns the slopes of the  $\log x/m$ — $\log p$  curves. The slopes are equal in the case of each vapour irrespective of the adsorbent. The slope of the  $\text{CCl}_4$  curve is very close to  $2/3$ , whilst that of the alcohol curves is about  $0.2$ . If the previously expressed view of the author regarding the classical equation (*J. Phys. Chem.*, 1945, **49**, 442) is correct, one has to conclude that the carbon tetrachloride molecules may be strictly confined to a two-dimensional space in the adsorbed state. The fact that the theoretical and the observed values of the slope agree so closely should be related to the observation that there is no initial anomaly i.e. a vertical rise of the  $x/m$ — $p$  curve at  $p \rightarrow 0$ , such

as is seen to occur with alcohol. One can therefore understand why the value of the slope in the case of alcohol is not significant. A part of the alcohol is obviously held by the gel very rigidly and is probably of the point-adsorbed type (*J. Phys. Chem.*, 1945, **49**, 442).

*Form of the Langmuir Isotherm at low Pressures*

Consider the slope of the Langmuir adsorption isotherm

$$x/m = \frac{\alpha\beta p}{1 + \beta p} \quad \dots \quad \dots \quad \dots \quad (1)$$

at the point  $p$ . The slope  $= \frac{d(x/m)}{dp} = \frac{\alpha\beta}{(1 + \beta p)^2} \dots \dots \dots (2)$

The rate of change of this slope at any pressure  $p$  is given by

$$\begin{aligned} \frac{d^2(x/m)}{dp^2} &= \frac{d}{dp} \left[ \frac{\alpha\beta}{(1 + \beta p)^2} \right] \text{ from (2)} \\ &= - \frac{2\alpha\beta}{(1 + \beta p)^3} \quad \dots \quad \dots \quad \dots \quad (3) \end{aligned}$$

We find from (3) that if the slope of the isotherm is small, it is most strongly curved near the origin. This result contradicts the usual statement that the isotherm should become linear as  $p$  approaches low values. This statement is based on an approximate reasoning adopted by Langmuir himself (*J. Amer. Chem. Soc.*, 1916, **38**, 2221).

A general expression for the radius of curvature  $r$  of the isotherm at a point  $p$  may be written down as

$$r = \frac{1 + \left[ \frac{d(x/m)}{dp} \right]^2}{\frac{d^2(x/m)}{dp^2}} \quad \dots \quad \dots \quad \dots \quad (4)$$

Substituting appropriate values from (2) and (3) in (4),

$$r = \frac{(1 + \beta p)^4 + \alpha^2 \beta^2}{2\alpha\beta^2 (1 + \beta p)^3}$$

neglecting the negative sign. One can see readily that the condition that  $r$  be a minimum *i.e.* the isotherm be curved most, is

$$p = \frac{\sqrt[4]{3\alpha^2\beta^3} - 1}{\beta} \quad \dots \quad \dots \quad \dots \quad (5)$$

It is quite possible therefore that the pressure at which the isotherm is curved most, may be close to the zero pressure, the actual value being determined by the constants  $\alpha$  and  $\beta$ . Large values of  $\beta$  are particularly unfavourable to the validity of Langmuir's relevant statement which is apparent from an examination of (1) itself.

It is seen from Fig. 2 that the isotherms have their strongest curvatures well within 50 mm. of oil (or 3 mm. of Hg). The isotherms therefore deviate most strongly from Henry's law within the range of these low pressures, but this fact by itself does not rule out the applicability of the Langmuir equation as may be found frequently stated in literature.

The fact that the deviations from straight line graphs in Fig. 3 are at least qualitatively in favour of the classical equation

$$x'_m = k \cdot p^{1/n} \quad \dots \quad \dots \quad \dots \quad (6)$$

is demonstrated from the following consideration. In obtaining the value of the slope of the

$\frac{p}{x/m} - p$  curve from (6) one gets

$$\frac{d}{dp} \left( \frac{p}{x/m} \right) = \frac{d}{dp} \left( \frac{p}{K \cdot p^{1/n}} \right) = \frac{n-1}{n} \cdot \frac{1}{x/m} \quad \dots \quad (7)$$

Equation (7) shows that the slope of the curve is not constant but decreases as the amount of adsorption increases *i.e.* as the pressure increases, which is the fact actually observed.

The experimental work described in this paper was carried out in the Chemical Laboratories of the University College, London. The author is grateful to Professor S. Sugden and the authorities concerned for the facilities provided. Part of this work has been abstracted from the author's Ph.D. thesis, London, 1947.

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*Received March 29, 1949.*

## INTERACTION OF ARABIC ACID WITH ACIDS AND NEUTRAL SALTS

BY S. N. MUKHERJEE AND A. C. BHOWMIK

Interaction of arabic acid with hydrochloric acid and neutral salts like NaCl and BaCl<sub>2</sub> has been studied. The results suggest the occurrence of exchange between the double layer round the micellar anions and those in the intermicellar liquid.

In a previous communication results of studies on the interaction of arabic acid with bases having cations of different valencies, both by potentiometric and conductometric methods have been reported (Mukherjee and Ghosh, this *Journal*, 1949, **26**, 277). The potentiometric titration curves have been observed to present the characteristics of a strong monobasic acid, while the conductometric ones show two inflexions : one corresponding to the neutralisation of the free acidity and the other to the total acidity with each of the bases studied. The total acidity was not constant but varied with the nature of the bases used for interaction in the order : Ca(OH)<sub>2</sub> > Ba(OH)<sub>2</sub> > KOH > NaOH. Results of conductometric and potentiometric methods, as followed in this case, however, showed excellent agreement amongst themselves.

This variation of the total acidity might be the result of a base exchange process going on at the surface of the micellar anions (arabate ion) as suggested in the previous communication (*loc. cit.*). In the present investigation an attempt has been made to throw more light on this aspect by studying the interaction of neutral salts with this acid in the expectation that, if there be any base exchange proceeding in this system, it will show the effect of the same with neutral salts also having cations of different valencies.

### EXPERIMENTAL

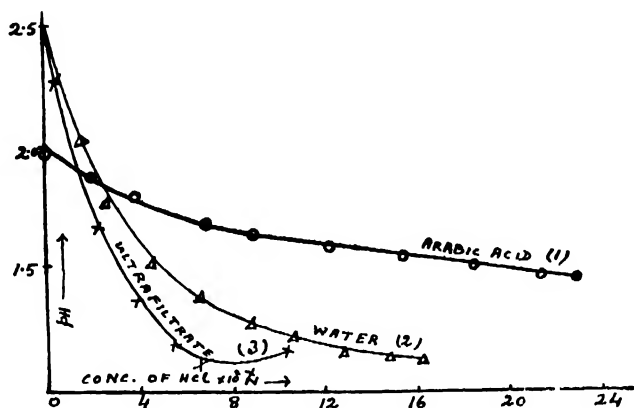
The acid and the salts used in this connection were of Merck's guaranteed reagent quality and were dissolved in equilibrium water of specific conductance  $1.2 \times 10^{-6}$  mho at 35°. The arabic acid solution had a concentration of 4 g. per 100 c.c. of the solution and was prepared by electrodialysis (*cf.* Thomas and Murray, *J. Phys. Chem.*, 1928, **32**, 676) of a specimen of gum arabic (B.D.H.) purified by the method of Bungenberg de Jong (*Koll.-Chem. Beih.*, 1938, **47**, 254). The solution so prepared corresponded with sol T mentioned in the previous communication (*loc. cit.*). Measurements were all carried out in a thermostat kept at  $35 \pm 0.1^\circ$ .

#### *Interaction with Acids*

The interaction of arabic acid with other acids was studied only in the case of HCl by noting the influence of this on the hydrogen-ion activity alone measured by the potentiometric method. A concentrated solution of HCl solution was added dropwise to the arabic acid solution and the  $p_H$  of the resulting mixture ascertained after each addition by the use of the hydrogen electrode. The maximum concentration of HCl did not exceed 0.24*N* in the

mixture. The arabic acid concentration in all measurements in this connection as well as for studying the interaction of neutral salts was 4 g. of the acid per 100 c.c. of the solution. A blank or control experiment was done by noting the changes in  $p_H$  when corresponding amounts of the same HCl solution were added to a volume of water equal to that of arabic acid solution used. The ultrafiltrate derived from the same arabic acid solution by passing it through a cello membrane (No. 600) was also tested in the same way with HCl solution. Results have been graphically presented in Fig. 1.

FIG. 1



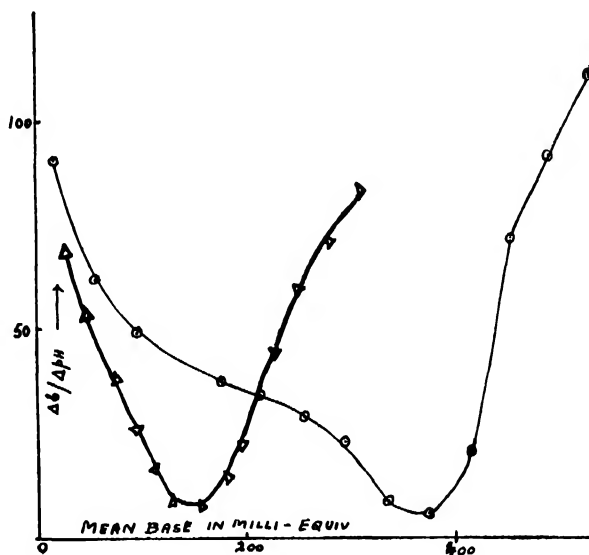
Of the three systems presented herein the arabic acid solution shows the least change in  $p_H$ . This therefore appears to possess some buffer mechanism within it, which works even with the addition of considerable amounts of hydrochloric acid.

The ultrafiltrate, on the other hand, shows a marked diminution of  $p_H$  when the amount of HCl added is small. At higher concentrations of HCl the  $p_H$  shows a slight but a well marked tendency to rise indicating a decrease in H-ion activity. The general picture of the change in  $p_H$  in the case of the ultrafiltrate resembles more closely the case of water than that of the arabic acid when small amounts of HCl were added.

The buffering mechanism of the arabic acid is not quite clear but it is possible to explain this if we assume that, in the arabic acid solution, the "arabate" ions remain as colloidal micelles round which there remains a layer of oppositely charged hydrogen ions bound, in consequence of which the H-ions in the former cannot register their activity by the potentiometric method. With increasing addition of HCl a considerable portions of the H-ions added become bound and only a part remains free to register their activity by slowly diminishing the  $p_H$ . In the ultrafiltrate the number of arabate ions is much fewer as shown by Mukherjee and Ghosh (this *Journal*, 1949, **26**, 277). Hence with increasing addition of HCl the hydrogen ions are not retained bound to the same extent as in the parent solution. With increasing addition of HCl the anions aggregate probably due to the partial neutralisation of their electrical charge, which the adsorption of H-ions eventually brings about and the bigger micelles subsequently take up a larger number of H-ions, in consequence of which the  $p_H$  of the solution tends to show a slight increase, as in the latter part of the curve. This increase in size of the particles is warranted by the observation that at high acid concentrations both

the parent solution and its ultrafiltrate develop turbidity and the former tends to coagulate at very high acid concentrations.

FIG. 1A



The buffer capacity curves for both the parent solution and the ultrafiltrate have been worked out by potentiometric titration of these with NaOH by plotting  $db/dp_H$  against mean base in milliequivalents and presented in Fig. 1A. Both present but one inflexion in their titration curves as referred to in an earlier paper (vide Mukherjee and Ghosh, *loc. cit.*). These inflexions have been shown in the buffer capacity curves as well, but there appears to be one important point where the curves differ from each other. The curve for the parent solution shows a flat portion in the region of half neutralisation, whereas this part is not quite marked in the curve for the ultrafiltrate. The difference in the behaviour of these in their interaction with hydrochloric acid may be suitably linked with the difference in their buffer capacity curves for a probable explanation.

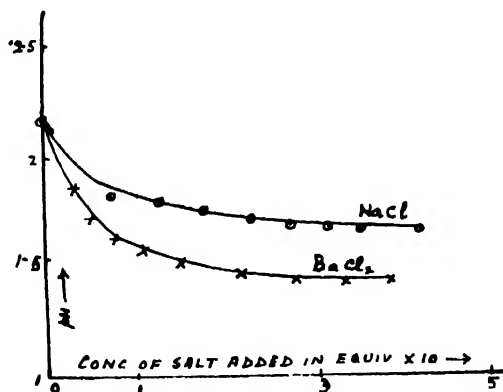
#### *Interaction with Neutral Salts*

Variations of hydrogen-ion activity, chlorine-ion activity and specific conductance have been studied with increasing addition of NaCl and  $BaCl_2$  solutions to a 4% arabic acid solution both by potentiometric and conductometric methods. In each case a control experiment was carried out by the addition of corresponding amounts of the salts to water.

**Hydrogen-ion Activity.**—Fig. 2 shows that neutral salts do bring about changes in the hydrogen-ion activity of the arabic acid solution.  $BaCl_2$  shows a greater depression of  $p_H$  than NaCl at corresponding concentrations. No blank experiment with water or HCl was done in this case because it is well known that neutral salts like NaCl or  $BaCl_2$  cause little change in hydrogen-ion activity and the behaviour is quite different in nature from that

observed in the present case.\* Increase in hydrogen-ion activity with addition of these neutral salts must therefore be the consequence of base exchange brought about by the cations, Ba being more effective than Na. The greater total acidity observed with  $\text{Ba}(\text{OH})_2$  in potentiometric and conductometric titrations of the arabic acid solutions as reported in an earlier

FIG. 2.



communication (*loc. cit.*) may thus be an outcome of greater efficiency of Ba ions to increase H-ion activity of the solution by replacement from the double layer surrounding the micellar anions.

FIG. 3

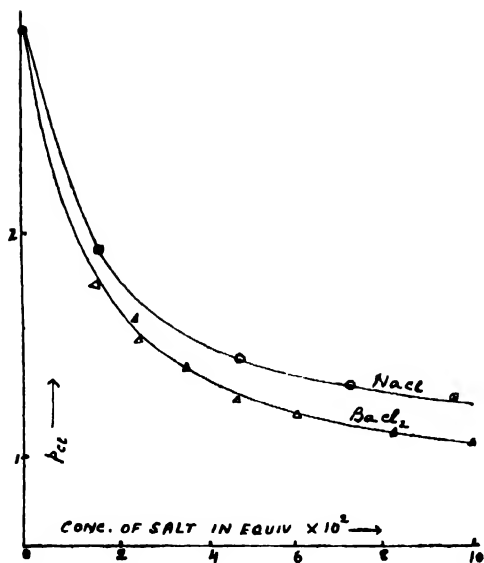
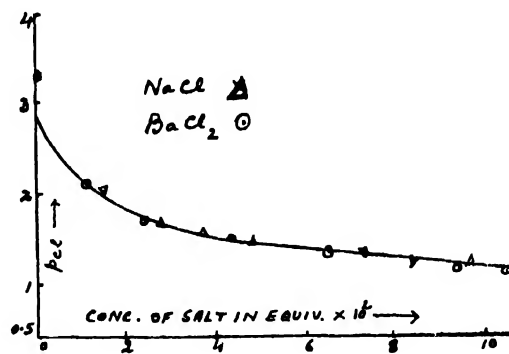


FIG. 4



\* For effect of neutral salts on the hydrogen-ion activity of water and HCl vide Harned "Physical Chemistry of Electrolytic Solution," Reinhold Publishing Corpn. 1943, p. 487 and pp. 450-60 respectively.



**Chlorine-ion Activity.**—Variations in the activity of the chlorine ions were also studied and graphically represented in Fig. 3, by plotting  $p_{Cl}$  ( $-\log a_{Cl}$ ) against concentrations of the neutral salts added. Chlorine-ion activity was measured by silver-silver chloride electrode prepared by the method of Noyes and Ellis (*J. Amer. Chem. Soc.*, 1917, **39**, 2532) and standardised against a standard NaCl solution (cf. Harned "Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., 1943, p.557) of known chlorine-ion activity at 35°.

A blank experiment with water alone for purposes of comparison was performed with both the salts and the results shown in Fig. 4. The graphs for  $p_{Cl}$  against salt concentrations (NaCl and BaCl<sub>2</sub>) are overlapping throughout the course studied which signifies that the chlorine-ion activities of NaCl and BaCl<sub>2</sub> solutions at corresponding concentrations of these salts, expressed in equivalents, are almost identical at least in dilute solutions.

But when these salts are added to the arabic acid solution, BaCl<sub>2</sub> shows a greater Cl-ion activity than NaCl at corresponding equivalent concentrations (vide Fig. 3).

**Specific Conductance**—Blank experiments for BaCl<sub>2</sub> and NaCl added to water is graphically shown in Fig. 5. Both these salts at the same concentrations show difference in specific conductance naturally due to a difference in their ionic conductance, Ba-ion having a greater conductance ( $L_{Ba} = 55$  mho at 18°) than Na-ion ( $L_{Na} = 43.16$  at 18°). When, however, these salts are added to the 4% arabic acid solution, the difference in specific conductance disappears almost entirely and the plots for the sp. conductance for the two salts run nearly coincident as shown Fig. 6.

FIG. 5

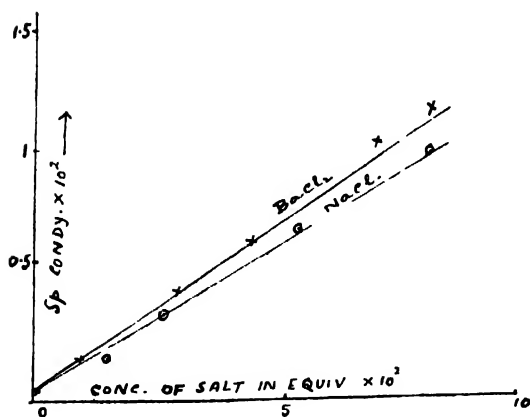
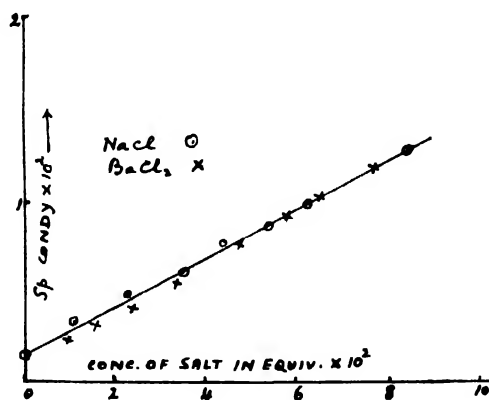


FIG. 6



This observation is interesting and suggestive. If we assume that both Na and Ba ions, when added in small quantities to a fairly concentrated solution of arabic acid (4% in the present case), can replace H-ions bound in the double layer and these H-ions can register their conductance in place of the added Ba or Na ions whose influence, though not entirely obliterated, is but small, we can find an explanation to this peculiar observation noted above.

## C O N C L U S I O N S

Thus it appears that there is in all probability some type of base exchange going on in this system and the Ba-ion is more effective than the monovalent Na-ion. In this respect the present observations tally with those made in other systems by different workers (Mukherjee, Mitra and Mukherjee, *Trans. Nat. Inst. Sci. India*, 1937, **1**, 227, *et seq.*) so far as base exchange is concerned, because divalent ions like Ba have been generally observed to show greater base exchange capacity than monovalent ions like Na.

In the light of these conclusions it is now easy to understand why  $\text{Ba(OH)}_2$  should register greater total acidity than NaOH as observed previously (Mukherjee and Ghosh, *loc. cit.*).

Grateful thanks of the authors are due to Dr. J. N. Mukherjee, Director of the Indian Agricultural Research Institute, New Delhi, for his kind interest and helpful suggestions in connection with this piece of work.

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## STUDIES IN SESQUITERPENES. PART VII. ON THE IDENTIFICATION OF $\beta$ -CARYOPHYLLENE

BY SUKH DEV AND P. C. GUHA

The importance of the blue nitrosite in the identification of  $\beta$ -caryophyllene has been pointed out and some of its derivatives have been prepared.

The mixture of hydrocarbons, known as the caryophyllenes, occurs quite widely distributed in nature ("Handbuch der Pflanzen-analyse", dritter Band /erste Hälfte, spezielle Analyse II, p.604, 1932 Ed.). Deussen (*Annalen*, 1907, **356**, 1) was the first to recognise that the sesquiterpene "caryophyllene" is not a homogeneous substance. A prolonged series of investigations has led Deussen and co-workers (*Annalen*, 1907, **356**, 1; 1908, **359**, 245; 1909, **369**, 51; 1912, **388**, 136; *J. prakt. Chem.*, 1911, ii, **83**, 483; 1914, **90**, 324; 1926, **114**, 63; 1927, **117**, 273; 1928, **120**, 133; 1929, **122**, 261) to conclude that caryophyllene contains two, and very probably three hydrocarbons, viz.,  $\alpha$ -caryophyllene,  $\beta$ -caryophyllene and  $\gamma$ -caryophyllene or *isocaryophyllene*. The work of Ruzicka and Wind (*Helv. Chim. Acta*, 1931, **14**, 410) has rendered the homogeneity of  $\gamma$ -caryophyllene, also doubtful.

Only a very partial separation of these sesquiterpenes can be effected by fractional distillation, and the evidence which Deussen has advanced for their individual existence is based on the isolation of a number of crystalline derivatives originating from different hydrocarbons (Deussen, *Annalen*, 1912, **388**, 136).

Of the various derivatives available for the characterisation of  $\beta$ -caryophyllene (Deussen, *loc. cit.* *J. prakt. Chem.*, 1914), the blue nitrosite holds a unique position. The nitrosochloride is not very suitable, since whenever an attempt is made to obtain a nitrosochloride from a hydrocarbon fraction rich in  $\beta$ -caryophyllene, always a mixture of nitrosochlorides is obtained from which the isolation of  $\beta$ -caryophyllene nitrosochloride is very laborious and often fails; in dealing with a mixture of  $\alpha$ -caryophyllene and  $\beta$ -caryophyllene, which usually accompany each other, the mere recrystallisation of the crude nitrosochloride leads to the isolation of  $\alpha$ -caryophyllene nitrosochloride, even though in the original mixture the  $\beta$ -caryophyllene may be predominating. The caryophyllene dihydrochloride can be obtained from both  $\beta$ - and  $\gamma$ -caryophyllene. It is not clear whether the  $\beta$ -caryophyllene alcohol originates only from  $\beta$ -caryophyllene or can also be obtained from the  $\gamma$ - and  $\alpha$ -varieties. In contrast to all this the blue nitrosite is known to originate definitely from  $\beta$ -caryophyllene and can be very easily prepared and purified.

During the identification of  $\beta$ -caryophyllene, isolated from *Hardwickia pinnata* oil, it was observed that the melting point of the blue nitrosite cannot be raised beyond  $110^\circ$ , though Deussen has reported a m.p. of  $115^\circ$  (*Annalen*, 1907, **356**, 13). Since the difference in the m.p. is appreciable, we were, at first inclined to the view that the nitrosite from the *Hardwickia pinnata* oil might be different from  $\beta$ -caryophyllene nitrosite. As a result of further investigations it has become clear that the m.p.  $110^\circ$  is the correct m.p. of  $\beta$ -caryophyllene nitrosite. A sample of  $\beta$ -caryophyllene nitrosite prepared from genuine caryophyllene (B.D.H.) also melted at  $110^\circ$  and the mixed m.p. with the sample prepared from the oil of *H. pinnata* was

undepressed. This has been confirmed by Simonsen\* (*private communication*). He has stated that the m.p. of our product (a sample was sent to him) when introduced in a bath at 100° was 112° and that the mixed m.p. with an authentic sample was the same. It has been observed by us also that the m.p. of the nitrosite depends to some extent on the rate of heating. When the temperature is raised rapidly, the substance melts at about 112°, but on raising the temperature of the bath slowly towards the end (the correct procedure for finding out m.p.) the substance always melts at 110°.

*Derivatives of the Nitrosite.*—Because of the importance of this blue nitrosite in the characterisation and identification of  $\beta$ -caryophyllene, the properties of the nitrosite have been examined. The very high optical rotation of the nitrosite (+1661) is quite characteristic. The nitrosite is not soluble in aqueous alkali, hot or cold, indicating thereby that the nitrosite is a true nitroso compound and does not isomerise to the oxime form. It reacts easily with strong bases to yield characteristic nitrolamines. The *nitrol-piperidide* and *nitrol-benzylamine* have been prepared. The nitrosite easily reacts with *iodine* giving a very characteristic crystalline compound. The *hydrochloride* obtainable by passing hydrochloric acid gas through an ethereal solution of the nitrosite is also a useful derivative. The melting points of these compounds are recorded in the following table.

Compound.	M.p.	M.p. as given in the literature.
Nitrosite	110°	115° *
Nitrolbenzylamine	172-73°	172-73° *
Nitrolpiperidine	156-57°	
Hydrochloride	138°	137°*, 140°†
"Todo-nitrosite"	126°	125°†

Doussen (*Annalen*, 1912, **388**, 136).

†† Doussen (*J. prakt. Chem.*, 1914, *ii*, **90**, 324)

## EXPERIMENTAL

The blue nitrosite was prepared from the  $\beta$ -caryophyllene fraction of *Hardwickia pinnata* oil (Sukh Dev and Ghua, this *Journal*, 1949, **26**, 263), and was obtained in blue needles, m.p. 110° with effervescence;  $[\alpha]_D$ , +1600° (c, 1.24% in chloroform).

*Nitrolbenzylamine.*—To 0.5 g. of nitrosite, benzylamine (1.5 g.) was added. The mixture was heated on a water-bath for one and-a-half hours. The blue colour disappeared and the colorless solution was cooled, when the compound crystallised out. Alcohol (3 c.c.) was added to it and boiled to dissolve the crystals and allowed to crystallise slowly. The product was once recrystallised from alcohol and once from chloroform-alcohol mixture and was obtained as white, silky needles, m.p. 172-73° with previous shrinking.

*Nitrolpiperidine.*—A mixture of the nitrosite (1.0 g.), piperidine (1.0 g.) and alcohol (10 c.c.) was refluxed for half an hour and allowed to cool. Water was added till a turbidity just appeared. This was again heated to obtain a clear solution and allowed to

The authors' sincere thanks are due to Prof. J. L. Simonsen, F. R. S. for taking a mixed m. p. of their nitrosite with his own sample.

crystallise slowly. The product was recrystallised from alcohol several times till the m.p. became constant. It was obtained as white, prismatic needles, m.p.  $156-57^{\circ}$  (the m.p. depends on the rate of heating, by quick heating it melts above  $158^{\circ}$  while by slow heating, below  $155^{\circ}$ ). (Found : N, 8.6.  $C_{20}H_{34}ON_2$  requires N, 8.8 per cent).

*Nitrosite Hydrochloride*.—The blue nitrosite (1.0 g.) was dissolved in dry ether (7 c.c.). The solution was chilled to  $-20^{\circ}$  and saturated with a rapid current of dry hydrochloric acid gas. The hydrochloride started separating out towards the end. The bluish green reaction mixture was worked up by removing the solvent and the excess gas in vacuum in a minute current of dry air. The residue was recrystallised from ethyl acetate till the m.p. became constant (two crystallisations). The product was obtained as blue needles, m.p.  $138^{\circ}$  with effervescence, yield 80%.

*"Ido-nitrosite"*.—The nitrosite (1.4 g., 0.05M) was dissolved in 5 c.c. of chloroform and iodine (0.5 g., 0.041 atom eq.) dissolved in warm chloroform (15 c.c.) was introduced in three lots to the nitrosite solution with shaking. The mixture was then allowed to remain at room temperature with occasional shaking. The iodine colour was slowly discharged and when the colour had faded out to a pale brown (four hours), the solution was poured in a dish and the solvent allowed to evaporate during several hours. The residue on trituration with a little ethyl acetate became solid. It was recrystallised from ethyl acetate (5 c.c.). The product was obtained as stout, transparent, hexagonal prisms, yield 1.0 g., m.p.  $126^{\circ}$ , (these can be obtained several cm. long and several mm. thick by slow crystallisation), orange-red in colour (the colour depends on the size of the crystals, by quick crystallisation, small, practically colorless crystals can be obtained. The large red crystals give a practically white powder on crushing).

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## KINETICS OF HALOGENATION OF FATTY ACIDS PART I. IODINATION OF ACETIC ACID

BY MIHIR NATH DAS AND SANTI R. PALIT

The kinetics of iodination of sodium acetate dissolved in glacial acetic acid have been measured at 35° and 25° for sodium acetate concentrations between 0.01 *M* and 1.0 *M* and for iodine concentrations between 0.01*M*—0.05*M*. The reaction rate is found to be nearly bimolecular at the beginning but falls off very rapidly owing to the inhibiting effect of the iodide ions formed during the reaction and also to the opposition caused by the back reaction. The value of  $k_2$  tends to increase with decrease of acetate concentration and lies in the range  $1.2$  to  $1.6 \times 10^{-2}$  mol<sup>-1</sup> litre<sup>-1</sup> min<sup>-1</sup>. The energy of activation is of the order of 25,000 calories.

Among lithium, sodium and potassium acetates the speed of reaction is in the order : K > Na > Li, which is also the order of the conductivities of these solutions.

It is surmised that the acetate ion is being iodinated and iodine being an electrophilic reagent, the reaction is favoured by the concentration of negative charge round the  $\alpha$ -carbon atom owing to repulsion of electrons from the negative ionic charge at the carboxylate end.

A considerable amount of work has been done on the  $\alpha$ -halogenation of saturated aliphatic acids with a view to explaining the mechanism of the reactions involved (Steiner, *Ber.*, 1874, **7**, 184; Lapworth, *J. Chem. Soc.*, 1904, **85**, 41; Aschan, *Ber.*, 1912, **45**, 1913; 1913, **46**, 2162; Ward, *J. Chem. Soc.*, 1922, **121**, 1161; 1923, **123**, 2207; Watson, *J. Chem. Soc.*, 1925, 2067; *Chem. Rev.*, 1930, **7**, 173; Hell and Urech, *Ber.* 1880, **13**, 531; Waston, *et al.*, *J. Chem. Soc.*, 1929, 1373; 1928, 2779). This has, however, been mostly restricted to bromination and chlorination at somewhat elevated temperatures, and usually in presence of catalysts. Very little information, however, is available on the iodination of carboxylic acids. This is, no doubt, due to the relative inactivity of elementary iodine in direct substitution reactions. As a general rule, direct iodination, especially at ordinary temperature, is rather rare and only a very few types of organic compounds are found to undergo direct iodine substitution with any measurable speed at room temperature. Carboxylic acids are, in general, quite stable towards this element even at fairly high temperatures. Watson and Roberts found no reaction to occur when acetic acid was heated with iodine at 100° (*J. Chem. Soc.*, 1928, 2779). It has long been known that solutions of iodine in glacial acetic acid can be preserved unchanged for any reasonable length of time and even iodine monochloride, which is a much stronger iodinating agent than iodine itself, has got no appreciable action on glacial acetic acid, which is actually used as a solvent for this reagent (Wij's solution). Bromine and chlorine also do not react with saturated aliphatic acids unless at somewhat elevated temperatures, and many investigators have actually used glacial acetic acid as the medium of reactions involving bromine and iodine (Bartlett and Vincent, *J. Amer. Chem. Soc.*, 1933, **55**, 4993; Nazaki and Ogg, *ibid.*, 1942, **64**, 697; Robertson and co-workers, *J. Chem. Soc.*, 1938, 179; 1933, 1323; 1937, 337 *et seq.*)

In spite of this inactivity of the carboxylic acids towards halogens, in general and iodine, in particular, it has been observed by one of the authors (Palit) and has already been reported

in course of a previous note (Das, *Science & Culture*, 1948, **14**, 165) that a solution of sodium acetate in glacial acetic acid, or propionate in propionic acid and similar systems react with iodine dissolved in the same solvent and that the reaction proceeds with a measurable speed at ordinary temperature. Bromine also reacts in a similar way and more readily than iodine. We have undertaken a detailed study of this reaction with a view to finding out the general characteristics and to elucidating reaction mechanism. The present paper reports the results of a preliminary study of the acetate-acetic acid-iodine system.

It may be mentioned in this connection that iodine has also been found to react with a solution of sodium acetate in glycol, but in this case, it is not known with certainty as to whether the acetate or the glycol is being iodinated, as there is every possibility that glycol itself, though it normally remains practically unaffected by iodine, may react with iodine under the catalytic influence of the acetate. We have therefore chosen acetic acid as the solvent in order to eliminate this uncertainty. We have concerned ourselves mainly with the following physicochemical aspects of the reaction:—

- (i) Light sensitiveness
- (ii) Effect of concentration of the reactants
- (iii) Effect of temperature
- (iv) Effect of other acetates
- (v) Effect of water
- (vi) Effect of added salts
- (vii) Effect of medium.

#### EXPERIMENTAL

*Materials.*—Sodium acetate was twice recrystallised from water and the crystals were subsequently fused. The fused mass was preserved in a desiccator. Iodine was purified by resublimation over potassium iodide. Glacial acetic acid was partially frozen out and the solid fraction was distilled over 'drierite'. Solutions of iodine in the acetic acid so purified were found to give constant titre values against thiosulphate over a considerable length of time (more than two weeks).

Experiments were carried out at two temperatures, 25° and 35°. The thermostat used for the purpose maintained a constant temperature throughout and maximum variations were within  $\pm 0.05^\circ$ .

Glass-stoppered bottles were used for the reactions. Five c.c. of reaction mixtures were pipetted out, at definite intervals, into 50 c.c. of water in which potassium iodide was dissolved, in order to arrest the reaction as also to keep the iodine in solution. Titrations were done with  $N/100$  standard thiosulphate solution with starch as indicator. Freshly boiled water, well cooled, was used for the purpose. Experimental results were checked and found to be fairly reproducible.

Concentrations of the acetate were varied between the limits  $0.01M$ — $1.0M$ , but mostly we used rather high concentrations ( $0.4M$  to  $1.0M$ ) to maintain the salt effects more or less constant, and also because at such high concentrations of the acetate the reaction was fairly fast and thus convenient for measurements of iodine consumption.

Iodine concentrations were varied between the limits  $0.01M$ — $0.05M$ , the higher limit being determined by the low solubility of iodine in glacial acetic acid. Further lower concentrations of iodine could not be investigated owing to experimental difficulties. With very low concentrations of iodine, reproducible results could probably be obtained only by the total exclusion of atmospheric oxygen and estimation by colorimetric methods, which we have not done so far.

To economise space we reproduce here only the results obtained with relatively high concentrations of the acetate, the iodine concentrations being restricted to two values. Direct titre values in c.c. of  $0.991N/100$ -thiosulphate are given, a typical run in each case being chosen for the purpose. At the foot of each column are given the corresponding values of  $k_2$  (bimolecular constant) calculated from both sets of experiments (which were mostly done in duplicate).

TABLE I

*Change of thiosulphate titre with time in presence of diff. conc. of NaAc at 35°.*  
Conc. of iodine =  $0.0241M$ .

Time.	$1.0M$ -NaAc.	$0.8M$ -NaAc.	$0.6M$ -NaAc.	$0.4M$ -NaAc.
0 min.	24.30	24.30	24.30	24.30
10	21.85	22.40	22.52	23.10
20	20.70	21.20	21.62	22.46
30	20.05	20.50	21.22	21.96
45	19.30	20.80	20.40	21.36
60	18.80	19.30	19.92	20.96
90	18.10	18.60	19.12	20.15
120	17.75	18.10	18.70	19.65
180	17.10	—	18.04	19.00
24 hours	15.90	16.95	16.35	16.62
$k_2 \times 10^2$ (litres/g. mole min.)	1.28	1.15	1.34	1.56
	1.16	1.15	1.54	1.56

TABLE II

*Iodine and sodium acetate at 35°.*  
Conc. of iodine =  $0.01205M$ .

	$1.0M$ -NaAc.	$0.8M$ -NaAc.	$0.6M$ -NaAc.	$0.4M$ -NaAc.
0 min.	12.15	12.15	12.15	12.15
10	10.95	11.10	11.20	11.50
20	10.35	10.50	10.72	11.14
30	9.80	10.14	10.42	10.96
45	9.45	9.70	10.02	10.60
60	9.10	9.36	9.76	10.36
90	8.80	9.08	9.30	10.02
120	8.50	8.74	9.04	9.66
180	8.30	8.38	8.62	9.28
24 hours	7.85	8.06	8.08	8.10
$k_2 \times 10^2$ (litres/g. mole min.)	1.17	1.41	1.61	1.66
	1.24		1.61	1.68



TABLE III

*Iodine and sodium acetate at 25°*

Time	0.8M-NaAc + 0.01205M-I <sub>2</sub>	0.4M-NaAc + 0.01205M-I <sub>2</sub>
0 min.	12.15	12.15
10	11.82	12.06
20	11.50	11.86
30	11.25	11.72
45	10.92	11.52
60	10.72	11.30
90	10.30	11.10
120	9.98	10.85
180	9.60	10.54
24 hours	8.30	8.18
$k_1 \times 10^2$ (litres/g mole min.)	0.35 0.33	0.41 0.41

TABLE IV

*Effect of other alkali metals.*

Temperature = 35°

Time	1.0M-KAc + 0.01205M-I <sub>2</sub>	0.4M-LiAc + 0.0241M-I <sub>2</sub>
0 min.	12.15	24.30
10	10.12	23.30
20	9.38	22.75
30	8.90	22.50
45	8.60	22.02
60	8.34	21.65
90	8.18	21.04
120	8.04	20.60
180	7.78	19.90
24 hours	7.40	17.0
$k_2 \times 10^2$ (litres/g. mole min.)	2.17 2.24	1.27

As will be seen from above, the reaction rate rapidly falls off with progress of time. This is not only due to the gradual consumption of iodine in course of the reaction, but also, in a greater measure, to the formation of tri-iodide (I<sub>3</sub>') with the iodide generated, which results in a decrease of the effective concentration of iodine. Addition of iodides, as expected, strongly retards the reaction. This is naturally a common feature of many reactions involving iodine in which the reaction rate depends on the iodine concentration. For a proper interpretation of the kinetics of the reaction, therefore, a knowledge of the tri-iodide equilibrium in glacial acetic acid is essential. This, however, involves enormous complications in the calculations which could be simplified to some extent by carrying out the reaction in presence of iodide added in excess (cf. Griffith and Mackewon, *Trans. Faraday Soc.*, 1932, **28**, 752; Nazaki and Ogg, *loc. cit.*). But at a relatively high concentration of iodide, the reaction becomes inconveniently slow for accurate measurements, and hence it was not possible to carry through in the above manner.

In addition to the tri-iodide formation, there is evidently another complicating factor involved here. The reaction is found to stop, for all practical purposes, in less than 24 hours (or 48 hours with low concentrations of reactants), and even with very high concentrations of acetate, the reaction is never found to reach completion. This has been amply verified by the fact that on keeping the reaction mixture at a constant temperature for two weeks at a stretch, no appreciable change in the titre value was observed after 2 days. All these observations tend to suggest that, in all probability, a state of equilibrium is reached at which the greater portion of the iodine remains unchanged.

*Light Sensitiveness.*—The reaction has been studied both in diffused daylight and in the dark, and no marked difference has been observed. No photochemical reaction therefore is involved here, at least so far as the visible region of the spectrum is concerned.

*Effect of Concentrations of Reactants.*—The reaction rate depends on the concentrations of both the reactants. The initial speed is approximately proportional to the first power of

the concentration of each reactant. The absence of exact proportionality is presumably due to the use of concentration terms instead of activity, incomplete dissociation of the acetate in glacial acetic acid which has got a rather low dielectric constant (6.13 at 20°), and also to kinetic salt effects which are naturally quite pronounced at the high acetate concentrations.

The dependence of the reaction rate on the iodine concentration is significant, when compared against the rate of halogenation of ketonic compounds, the latter reaction being zero-order with respect to iodine.

Attempts have been made to fit the experimental results in various kinetic equations, but without any success so far. This is due to the complicating factors discussed above, and hence the initial speed of the reaction has been graphically determined in the following way. The values of  $\Delta x/\Delta t$  (where  $x$  denotes the iodine consumed at time  $t$ ) for different values of the mean time were plotted against the mean time ( $t$ ) whereby a straight line was obtained for the first part of the reaction. On extrapolating the straight line so obtained,  $\Delta x/\Delta t$  at  $t=0$  was found out from the curve. From the value of  $\Delta x/\Delta t$  the velocity constant  $k$  was determined from the general equation for a bimolecular reaction :

$$\frac{dx}{dt} = k_2 [\text{Acetate}] [I_2]$$

For sodium acetate-iodine reaction at 35°, the values of  $k_2$  so obtained were found to lie in the range  $1.2 - 1.6 \times 10^{-2}$  litre/ g. mole. minute. As will be observed from the tables, this value

Fig. 1 (Upper half)

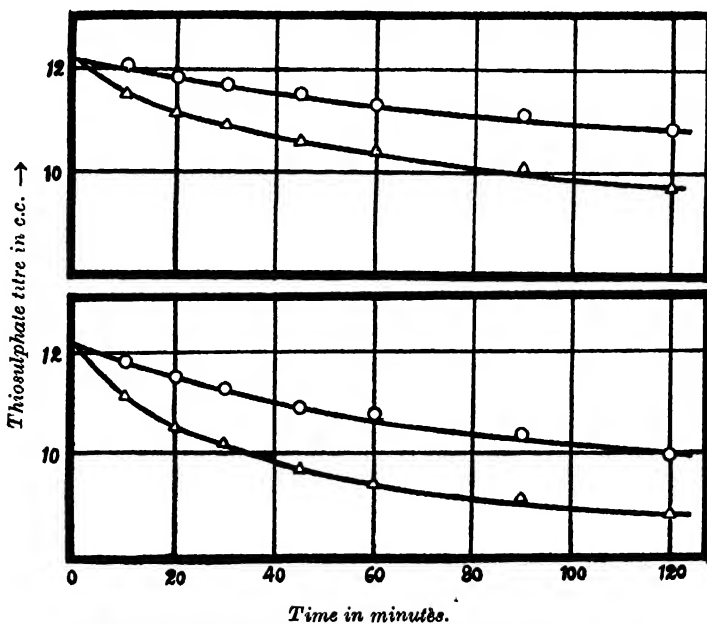


Fig. 1 (Lower half)

Upper curves : Reactions between 0.4*M*-sodium acetate and 0.01205*M*- $I_2$  at 25° (denoted by circles) and at 35° (denoted by triangles)  
 Lower curves : Reactions between 0.8*M*-sodium acetate and 0.01205*M*- $I_2$  at 25° (denoted by circles) and at 35° (denoted by triangles).

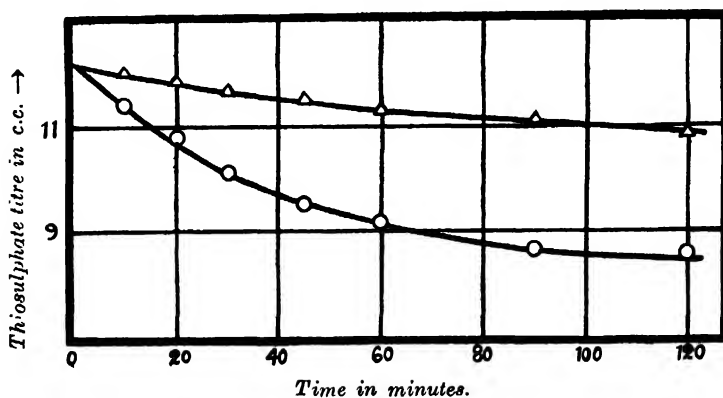
has got a tendency to increase with lower acetate concentrations. At  $25^\circ$ , the value of  $k_2$  lies in the range  $0.35-0.41 \times 10^{-2}$  (litre/g. mole. minute). The values of  $k_2$  so determined are shown in Tables I-IV, at the foot of the corresponding columns.

*Effect of Temperature.*—The reaction is much slower at  $25^\circ$  (curve I). Moreover, at the lower temperature, there appears to be a short time lag in the initial period, in which the reaction is very slow. The ratio of  $k^{35^\circ}/k^{25^\circ}$  calculated in the above manner was found to be in the neighbourhood of 4, which requires the energy of activation to be of the order of 25,000 g. cals.

*Effect of other Acetates.*—As evident from Table IV, the speed of the reaction is in the order  $\text{K} > \text{Na} > \text{Li}$ . The value of  $k_2$  for potassium acetate is found much higher (about 80 %) than that for sodium acetate under equivalent conditions, whereas the difference between lithium and sodium acetates is not so considerable. It is significant that this is in the same order as the conductivities of the respective acetates in glacial acetic acid medium (Kolthoff and Wilman, *J. Amer. Chem. Soc.*, 1934, **56**, 1014).

*Effect of Water.*—Very small amounts of water added to the reaction mixture are without any appreciable effect, but as the proportion of water is gradually increased, the speed steadily increases and the equilibrium is shifted towards the forward direction. The adjoining curve (Fig. 2) gives the comparative speeds at  $25^\circ$  of the reactions in glacial acetic acid and in 50% acetic acid, from which the pronounced difference will be evident. Reaction in such aqueous solvent is still under a more thorough investigation.

Fig. 2



Reactions between  $0.4M$ -Na acetate and  $0.01205M$ - $I_2$  at  $25^\circ$  in glacial acetic acid medium (denoted by triangles) and in 50% aqueous acetic acid medium (denoted by circles).

## DISCUSSION

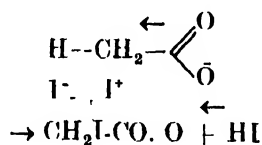
It is rather significant that though compounds containing ketonic carbonyl group readily undergo iodination at ordinary temperature, especially under the influence of acids and bases, carboxyl as also carboethoxy compounds are practically inert towards this element. This difference in behaviour of these compounds is easily understood, when viewed in light of the electronic mechanism of organic reactions.

The first step in the halogenation of ketonic compounds is a prototropic change which was first suggested by Lapworth (*J. Chem. Soc.*, 1904, **85**, 30) and has since been confirmed by

many investigators. Any such tautomeric tendency is, however, absent in mono-carboxylic acids, because that would lead to a loss in the resonance energy associated with the carboxyl group. The carboxylate ion possesses even higher resonance energy than the carboxyl group, though the exact value of this stabilising energy is not available (Pauling, "The Nature of the Chemical Bond", pp. 203-204). Any prototropic tendency must therefore be absent in the carboxylate ion as well.

Thus, tautomeric effect is of no significance in the substitution reaction we are studying and inductive effect plays an important role.

It is an established fact that the halogen molecules are polarised as  $X_2 = X^+X^-$  (Waters, "Physical Aspects of Organic Chemistry", pp. 167-68; Remick, "Electronic Interpretation of Organic Chemistry", pp. 55-56). There is definite evidence to show that the positive end of the halogen molecule is the active reagent, which naturally seeks that part of the substrate molecule at which the electron density is rather high. Halogenating agents are therefore electrophilic in character, and molecules containing electron-repelling groups, have got a tendency to undergo halogen substitution. Groups of the form  $-\text{CO}_2\text{R}$ , which include undissociated carboxyl groups in free carboxylic acids are electron-attractors (Hughes, *Trans. Faraday Soc.*, 1938, **34**, 185) and hence resist electrophilic substitution. The carboxylate ion, on the other hand, repels electrons due to the influence of the negatively charged oxygen atom :



The negative oxygen atom, through the operation of its own  $-I$  effect, tends to shift electrons towards the carbonyl carbon, which, in its turn transfers the effect to the methyl carbon atom. Thus, there is a local increase in the electron density at this  $\alpha$ -carbon portion of the molecule which attracts the reactive positive halogen ion, leading to substitution. This seems to account for the reactivity of the acetate ions towards iodination, as against the inactivity observed with undissociated acetic acid molecules.

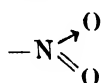
The above mechanism is further supported by the fact that undissociated phenols and phenolic ethers do not readily undergo halogenation, whereas phenoxide ions are readily halogenated (Hunter and Bundrow, *J. Amer. Chem. Soc.*, 1933, **55**, 2122; Soper and Smith, *J. Chem. Soc.*, 1926, 1582; 1927, 2756). It has also been found that salts of unsaturated acids (maleic etc.) add bromine and iodine more readily than the acids themselves (Berthoud and Mosset, *J. chim. phys.*, 1936, **33**, 271; Robertson, *J. Chem. Soc.*, 1937, 337). As both addition and substitution reactions with halogens occur primarily through a similar electronic mechanism (Ingold and Ingold, *J. Chem. Soc.*, 1931, 2354) these observations are quite in line with our arguments set forth above.

## STUDIES ON THE ELECTRIC POLARISATION AND STRUCTURE OF MOLECULAR COMPOUNDS. PART I

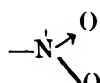
BY ROOP CHAND SAHNEY, RAM MITRA BERI, H. R. SARNA AND  
MAHAN SINGH

Total polarisation of the molecular compounds of *sym.*-trinitrobenzene, 2:4-dinitrophenol, 2:4-dinitro-1-chlorobenzene with hydrocarbons, phenols and amines have been measured and the results discussed in relation to the structure of the molecular compounds.

Lowry (*Chem. Ind.*, 1924, **43**, 218) has suggested that molecular compounds are formed by intermolecular co-ordination. Bennet and Wills (*J. Chem. Soc.*, 1929, 256) have supported the above view, pointing out that the deeper colour of the molecular compounds and the simple stoichiometric ratios in which the components are present are further evidence of the chemical linkage. The electronic formulation of these compounds is based on the suggestion that the nitro group with structure (I) is capable of acquiring structure (II) under certain conditions of activation.

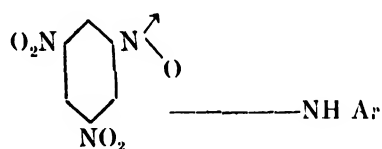


(I)

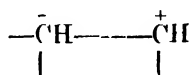


(II)

The nitrogen of the nitro group in the activated state can accept a pair of electrons from amino group of amines and the compound is thus represented as



In case of molecular compounds of trinitrobenzene with hydrocarbons, one of the double bonds of hydrocarbons acts in the polarised form as



and donates a pair of electrons for the co-ordinate linkage.

Recently, evidence has been adduced against the formation of these compounds through a semipolar bond. Absorption spectra of compounds of *m*-dinitrobenzene and picric acid with a number of hydrocarbons (Hunter, *J. Chem. Soc.*, 1936, 1576) indicated that they were merely superimposition of curves of two components and neither the position of maxima nor  $\log K$  indicated anything more than a small interaction. X-ray studies of *p*-iodoaniline-trinitrobenzene compound (Powell, *J. Chem. Soc.*, 1943, 153) showed that intermolecular distances were greater than 3.5 Å which excludes the possibility of any chemical bonds between molecules. Briegleb and co-workers (*Z. Physik*, 1932, **19**, 255 ; 1934, **26**, 63) after extensive investigations on the heats of interaction, dissociation and combination concluded that the forces involved in molecular compound formation were those of interaction between a strongly polar group of one component and induced dipole in the other. The electrostatic forces thus involved are intermediate between Van der Waal's forces of attraction and true co-valencies.

In view of the above it was considered desirable to make a detailed study of the dielectric polarisation of the molecular compounds. We have therefore determined the total polarisation of the compounds of *sym.*-trinitrobenzene, 2:4-dinitro-1-chlorobenzene, 2:4-dinitrophenol and picric acid with hydrocarbons, phenols and amines with a view to discussing their structures.

### EXPERIMENTAL

The molecular compounds of *sym.*-trinitrobenzene, 2:4-dinitrophenol and 2:4-dinitro-1-chlorobenzene were obtained by mixing the alcoholic solutions of the components in molecular proportions and boiling the mixture for a requisite time. The product was crystallised 3 or 4 times. Great care was taken to avoid any decomposition during crystallisation.

#### Total Polarisation Measurements

The dielectric constants of the solutions were determined on the heterodyne beat apparatus described before in a previous communication (this *Journal*, 1948, **25**, 285). The working of the apparatus was checked by making determinations on a number of standard substances of known values of dielectric constants. The densities of solutions were determined by means of a specific gravity bottle. The refractive indices of the solutions were measured on the Pulfrich refractometer using sodium lamp as a standard source of light. Benzene with  $\epsilon = 2.283$  at  $20^\circ$  was taken as the reference substance. The dielectric constants, molecular concentration, dipole moment and total polarisation of the components are given in Table I and those of the compounds with hydrocarbons in Table II, with amines in Table III, and with naphthols in Table IV.

TABLE I

No.	Name.	Mol. conc. ( $f_1$ )	Temp.	Dielectric constant.	Total polarisation $P_1$	Dipole moment (Debye unit).
1.	<i>m</i> -Dinitrobenzene	0.01071	293.2° A	2.513	329.6	3.743
2.	Picric acid	0.003860	293.0°	2.296	89.1	1.345
3.	2:4-Dinitrophenol	0.009549	293.0°	2.247	281.8	3.314
4.	2:4-Dinitro-1 chlorobenzene	0.008734	293.0	2.442	296.6	3.275
5.	Naphthalene	0.01368	293.4°	2.287	45.3	0.0
6.	Benzidine	0.004788	293.5	2.291	85.63	1.375
7.	$\alpha$ -Methylnaphthalene	0.002604	292.8	2.296	48.4	0.2296
8.	$\alpha$ Nitronaphthalene	0.005094	293.0	2.394	327.9	3.680
9.	Fluorene	0.010602	293.0°	2.286	54.7	0.28
10.	$\alpha$ -Naphthol	0.01217	292.8°	2.330	86.3	1.387
11.	$\beta$ Naphthol	0.01217	292.9°	2.331	88.77	1.412
12.	$\alpha$ -Naphthylamine	0.01227	292.6°	2.353	115.7	1.780
13.	$\beta$ -Naphthylamine	0.01227	292.5°	2.362	130.0	1.904
14.	<i>o</i> -Nitroaniline	0.006393	293.0°	2.469	430.80	4.231
15.	<i>m</i> -Nitroaniline	0.004575	293.0°	2.450	520.7	4.680
16.	<i>o</i> -Chloroaniline	0.01930	293.1°	2.376	95.48	1.773
17.	2:4:6-Trichloroaniline	0.00837	293.4°	2.351	154.10	2.168
18.	Phenanthrene	..	..	..	60.7	0.0*
19.	<i>sym.</i> -1:3:5-Trinitrobenzene	..	..	..	63.88	0.8*
20.	Bromonaphthalene	..	..	..	104	1.58*
21.	<i>m</i> -Chloroaniline	..	..	..	201	2.80*
22.	<i>p</i> -Chloroaniline	..	..	..	223	2.93
23.	<i>o</i> -Bromoaniline	..	..	..	104.4	1.77*
24.	<i>m</i> -Bromoaniline	..	..	..	187	2.65*
25.	<i>p</i> -Bromoaniline	..	..	..	227.5	2.99*
26.	<i>p</i> -Iodoaniline	..	..	..	199.4	2.82*
27.	Aniline	..	..	..	79.7	1.55*

\*The data for compounds 18 to 27 have been taken from the *Trans. Faraday Soc.*, 1934, **80**, Appendix.

TABLE II

*Polynitro compounds with hydrocarbons.*

No.	Name.	Mol. conc. (f)	Temp.	Dielectric constant.	Total polarisation ( $P_T$ ).	Dipole moment (Debye unit).
1.	<i>m</i> -Dinitrobenzene-naphthalene	0.002988	292.5 A	2.354	375.7	3.735
2.	<i>m</i> -Dinitrobenzene-benzidine	0.002514	292.5°	2.338	407.8	3.906
3.	<i>sym.</i> -Trinitrobenzene					
	—naphthalene	0.0025996	293.5'	2.289	76.93	0.8590
4.	Do — penanthrene	0.004526	293.0'	2.298	128.6	1.023
5.	Do — fluorene					
		0.006995	292.8'	2.299	111.5	0.8626
6.	Do — bromonaphthalene	0.004215	292.9	2.308	144.7	1.741
7.	Do benzidine	0.002327	292.7	2.294	150.4	1.626
8.	Do — $\alpha$ -methylnaphthalene	0.002327	293.4'	2.298	126.4	1.227
9.	Do — 1-nitronaphthalene	0.002277	293.0'	2.322	355.7	3.369
10.	Picric acid-naphthalene	0.002469	293.0°	2.921	121.5	1.148
11.	2:4-Dinitrophenol— $\alpha$ -naphthalene	0.005691	293.2°	2.367	279.7	3.022
12.	2:4-Dinitro-1-chlorobenzene— $\beta$ -naphthalene	0.002674	293.2'	2.337	347.8	3.450

TABLE III

*Polynitro compounds with animes.*

No.	Name.	Mol. conc. (f)	Temp.	Dielectric constant.	Total polarisation.	Dipole moment (Debye unit).
1.	<i>m</i> -Dinitrobenzene					
	naphthylamine	0.002846	292.8 A	2.359	442.8	3.956
2.	2:4-Dinitrophenol	0.002705	292.8	2.322	397.5	3.042
3.	2:4-Dinitro-1-chlorobenzene	0.002559	292.9	2.345	438.7	3.875
4.	<i>sym.</i> -Trinitrobenzene	0.002173	293.4'	2.292	128.8	1.811
5.	Do $\beta$ -naphthylamine	0.002483	293.0'	2.294	145.0	1.945
6.	Do — <i>o</i> -chloroaniline	0.002635	293.3'	2.311	212.5	2.597
7.	Do <i>o</i> -chloroaniline	0.005191	293.2	2.311	152.2	1.648
8.	Do <i>p</i> -chloroaniline	0.002635	293.4°	2.312	216.3	2.631
9.	Do — 2:4:6-trichloroaniline	0.004180	298.1	2.305	153.7	1.77
10.	Do <i>o</i> -nitroaniline	0.002495	293.3	2.362	546.4	4.466
11.	Do <i>m</i> -nitroaniline	0.002527	293.0	2.391	556.3	4.58
12.	Do — <i>o</i> -bromoaniline	0.00457	292.7'	2.305	140.1	1.753
13.	Do — <i>m</i> -bromoaniline	0.002277	292.6	2.306	228.3	2.649
14.	Do <i>p</i> -bromoaniline	0.002277	292.5	2.308	246.0	2.764
15.	Do — <i>p</i> -iodoaniline	0.002076	293.0	2.305	216.7	2.563
16.	2:4-Dinitrophenol — aniline	0.003192	292.7'	2.328	261.2	3.016

TABLE IV

*Polynitro compounds with naphthols.*

No.	Name.	Mol. conc. (f)	Temp.	Dielectric constant	Total polarisation ( $P_T$ )	Dipole moment (Debye unit)
1.	<i>sym.</i> -Trinitro-benzene— $\alpha$ -naphthol	0.004856	293.1°A	2.304	129.2	1.635
2.	Do— $\beta$ -naphthol	0.002484	293.0	2.293	124.8	1.512
3.	Picric acid— $\alpha$ -naphthol	0.002363	293.0	2.299	173.5	1.937
4.	Do— $\beta$ -naphthol	0.002363	293.0'	2.290	173.5	1.987
5.	2:4-Dinitro-1-chloro- benzene— $\alpha$ -naphthol	0.002548	292.5°	2.338	393.3	3.587
6.	2:4-Dinitro-1-chloro- benzene— $\beta$ -naphthol	0.002548	292.5	2.340	404.2	3.688

## D I S C U S S I O N

The following tables record the values of the additive and experimental total polarisation and their differences.

TABLE V

*Polynitro compounds with hydrocarbons*

No.	Substance.	Total polarisation		
		Additive sum.	Exptl.	Difference.
1.	<i>m</i> -Dinitrobenzene—naphthalene	374.9	375.5	— 0.60
2.	<i>m</i> -Dinitrobenzene—benzidine	415.23	407.8	+ 7.43
3.	<i>sym.</i> -Trinitrobenzene—naphthalene	109.18	76.93	+32.25
4.	<i>sym.</i> -Trinitrobenzene—phenanthrene	124.58	128.2	-- 3.62
5.	<i>sym.</i> -Trinitrobenzene—fluorene	118.58	111.5	+ 7.08
6.	<i>sym.</i> -Trinitrobenzene—benzidine	149.51	150.4	— 0.89
7.	<i>sym.</i> -Trinitrobenzene—bromonaphthalene	167.88	144.7	+ 23.18
8.	<i>sym.</i> -Trinitrobenzene—methylnaphthalene	112.28	126.4	— 14.12
9.	<i>sym.</i> -Trinitrobenzene—nitronaphthalene	391.78	355.7	+36.08
10.	Picric acid naphthalene	134.4	121.5	+12.9
11.	2:4-Dinitrophenol naphthalene	327.1	279.7	+47.4
12.	2:4-Dinitro-1-chlorobenzene—naphthalene	341.9	347.8	— 5.9

TABLE VI

*Polynitro compounds with naphthols.*

No.	Substance.	Total polarisation		
		Additive sum	Exptl.	Difference.
1.	<i>sym.</i> -Trinitrobenzene— $\alpha$ -naphthol	150.18	129.2	+ 20.98
2.	Do — $\beta$ -naphthol	152.65	124.8	+27.85
3.	Picric acid— $\alpha$ -naphthol	175.4	173.5	+ 1.9
4.	Do — $\beta$ -naphthol	177.87	173.5	+ 4.37
5.	2:4-Dinitro-1-chlorobenzene $\alpha$ -naphthol	382.9	393.2	— 10.3
6.	Do — $\beta$ -naphthol	385.37	404.2	— 18.83

TABLE VII

*Polynitro compounds with amines*

No.	Substance.	Total polarisation		
		Additive sum.	Exptl.	Difference.
1.	<i>m</i> -Dinitrobenzene $\alpha$ -naphthylamine	445.3	442.8	+ 2.5
2.	2:4-Dinitrophenol $\beta$ -naphthylamine	407.5	397.5	+10.0
3.	2:4-Dinitro-1-chlorobenzene $\alpha$ -naphthylamine	412.3	438.7	— 26.4
4.	<i>sym.</i> -Trinitrobenzene— $\beta$ -naphthylamine	179.58	128.8	+ 50.78
5.	Do — $\alpha$ -naphthylamine	193.88	145.0	+48.88
6.	<i>sym.</i> -Trinitrobenzene— <i>o</i> -chloroaniline	159.36	152.2	+ 7.16
7.	Do — <i>m</i> -chloroaniline	267.88	212.5	+ 55.38
8.	Do — <i>p</i> -chloroaniline	266.88	216.3	+ 50.58
9.	Do — trichloroaniline	217.98	153.7	+ 64.28
10.	Do — <i>o</i> -nitroaniline	494.68	546.4	— 51.72
11.	Do — <i>m</i> -nitroaniline	584.58	556.2	+ 32.28
12.	Do — <i>o</i> -bromoaniline	168.28	140.1	+ 28.18
13.	Do — <i>m</i> -bromoaniline	250.88	228.3	+22.58
14.	Do — <i>p</i> -bromoaniline	291.33	246.0	+45.38
15.	Do — <i>p</i> -iodoaniline	263.28	216.7	+46.58
16.	2:4-dinitrophenol—aniline	361.60	261.20	+100.38



With the exception of about half a dozen cases, these differences are quite big. They are both positive and negative. The total polarisation,

$P = P_0 + P_E + P_A + P_I + P_R$ , where  $P_0$ ,  $P_E$ ,  $P_A$ ,  $P_I$ , and  $P_R$  are orientation, electronic, atomic, ionic, and radical polarisations respectively.

The change in any of the constituents forming  $P$  will result in a change in the value of  $P$ . Therefore, in order to ascertain the cause of the change in the total polarisation on the formation of molecular compounds, we have tried to study and discuss the change due to each of the constituents of the total polarisation.

Orientation polarisation  $P_0$  is due to the unsymmetry of the molecules. When the centres of the positive and negative charges are not coincident, the molecule possesses a dipole moment equal to the product of the charge and their distance of separation. In the case of polynitro substances, orientation polarisation is due to the nitro group attached to the benzene or other hydrocarbon nuclei, the hydrocarbons themselves being non-polar. In the molecular compounds with hydrocarbons these polynitro compounds combine with the ring as a whole and no special group combination takes place. No change therefore takes place in the orientation polarisation in the case of molecular compounds of polynitro substances with hydrocarbons.

$P_E$  can be measured optically by means of refractive index (in the infra-red region), because the electromagnetic light waves can only cause the displacement of the electrons without affecting the atoms and the nuclei. Measurements of the electronic polarisation of the components and those of the molecular compounds show that there are no appreciable changes in the electronic polarisation on the formation of molecular compounds or in other words, electronic polarisation is not affected by the intermolecular changes accompanying the formation of the molecular compounds.

The remaining constituents forming the total polarisation are :  $P_I + P_A + P_R$ . The changes in the values of  $P_I$  are called interionic and those in the values of  $P_{AR}$  are called intermolecular changes of polarisation. In the case of heavier molecules the main contribution will be due to the ionic polarisation  $P_I^{AB}$  of the ions formed, and any intermolecular changes will be small compared with this term. Therefore, we may write as a first approximation for the differences of the vibrational polarisation term  $P(IAR)$  in the molecular compound formation.

$$P_{IAR} \equiv P_{IAR}^{AB} - (P_{IAR}^A + P_{IAR}^B) \simeq P_I^{AB}$$

if we neglect the small differences in the intermolecular terms.

Now let us consider how the change in the total polarisation is due to the ionic polarisation. In the formation of the molecular compounds, there is a change in the structure of the electronic clouds of the constituents, because the two constituents while entering as uncharged molecules, are transformed into ions in the molecular compounds. The surrounding field will now have a profound effect on the electronic clouds of these highly polarisable molecules. If the surrounding field has a positive charge, it will compact or harden the electronic clouds. On the other hand, if the surrounding field has a negative charge it will soften the electronic clouds of the nucleus, in which it is present. The general effect of the electric

field upon polarisation has been studied by Smyth, Born and Heisenberg. They have shown that the effective polarisation ( $P_{eff}$ ) in the presence of a strong field depends upon the polarisability ( $\alpha$ ) in the 'unstrained state' and the strength of the field. It is clear that  $\alpha$ -effective is greater than  $\alpha$  for positive charges and  $\alpha$ -effective is less than  $\alpha$  for negative charges.

Although it is possible to explain to a small extent both negative and positive differences of the polarisation of the molecular compounds from the sum of the components by the causes explained above, yet there are in most cases differences of a very high order. This indicates that there is some other phenomenon along with the above factors which is at work for such big polarisation differences. It therefore appears that in the formation of these molecular compounds, different resonance forms of the components take part in the compound formation. The extent to which a resonance form reacts depends upon the energy condition as well as the second reacting component.

For the quantitative treatment of the resonance structures and the effect of the rotational polarisation on the formation of molecular compounds, it was considered necessary to compare the dipole moments also of the above compounds with those of the additive sum of the components. These results will be described in the next communication.

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# ORGANIC FUNGICIDES. PART II. ON CERTAIN ETHERS OF CRESOTINIC ESTERS

BY A. B. SEN AND K. C. JOSHI

Several esters and ether-esters of cresotinic acids have been prepared.

Cavill, Vincent and Gibson (*J. Soc. Chem. Ind.*, 1947, **66**, 175) observed that esters and ether-esters of 4-hydroxybenzoic acid (*ibid.*, 1947, **66**, 274) possess good fungistatic activity. The present work was therefore undertaken to prepare analogous esters and ether-esters of *ortho*- and *meta*-cresotinic acids, which may also be expected to possess similar fungistatic activity.

The esters of *o*-cresotinic acid have been obtained by Schotten-Baumann's reaction by treating the acid chloride (obtained by the action of phosphorus pentachloride on the acid, suspended in petrol ether) with an excess of the requisite alcohol (Anschutz, *Ber.*, 1897, **30**, 223; Ansch, Schroeder, Weber and Ansprach, *Annalen*, 1908 **346**, 342). The esters of *m*-cresotinic acid have been obtained by Fischer's method by refluxing the parent acid with an excess of the requisite alcohol containing 3% hydrochloric acid gas as a catalyst. (Behal, *Bull. soc. chim.*, 1908, *iv*, **3**, 730; Pinner, *Ber.*, 1890, **23**, 2938).

The method used for the preparation of the ethers was an adoption of that described by Cavill and Gibson (*J. Soc. Chem. Ind.*, 1947, **66**, 274) who obtained these ethers by refluxing the sodium derivative of the hydroxy-esters with the appropriate *n*-alkyl iodide in absolute alcohol. The sodium derivative of the cresotinic acid-alkyl ester itself was obtained by the addition of the ester to an equivalent quantity of sodium ethoxide, dissolved in excess of absolute alcohol.

## EXPERIMENTAL

**2-Oxy-3-methylbenzoyl Chloride.**—2-Oxy-3-methylbenzoyl chloride was prepared by the method of Anschutz (*loc. cit.*) and Ansch *et al.* (*loc. cit.*) by treating *o*-cresotinic acid (100 g.) with  $\text{PCl}_5$  (165 g.) in petrol-ether (250 c.c.). The petrol-ether and  $\text{POCl}_3$  were removed and the residual liquid distilled under reduced pressure. It is a pale yellow liquid, b.p.  $202^\circ/5\text{mm.}$ , yield 102 g. (91.1% of theory) (Anschutz *et al.*, *loc. cit.* report m.p. 28).

**Esters of *o*-Cresotinic Acid.**—These esters were obtained by Schotten-Baumann's reaction by treating 2-oxy 3-methylbenzoyl chloride (1 mol.) with excess of the requisite anhydrous alcohol (4 mols.). The excess of the alcohol was removed, the residual liquid washed with cold 20% caustic soda solution and extracted with ether. The ethereal layer was washed with water, dehydrated over anhydrous sodium sulphate, the ether removed, and the residual liquid distilled under reduced pressure. The following compounds have been obtained.

TABLE I

Compounds.	Reactants.	Yield.	Boiling point obs.	Analysis.	
				Found.	Calc.
(1) 2-Oxy 3-methyl <i>isopropylbenzoate</i>	Acid chloride (20g.) <i>iso</i> Propyl alcohol (35 c.c.)	15 g. 68.0%	$194^\circ/5\text{ mm.}$	C, 67.68% H, 7.35	68.04% 7.22
(2) 2-Oxy 3-methyl <i>n</i> -butylbenzoate	Acid chloride (25 g.) <i>n</i> -Butyl alcohol (50 c.c.)	22 72.2	$175/7$	C, 68.76 H, 7.71	69.23 7.69

Besides, 2-oxy-3-methyl methylbenzoate and 2-oxy 3-methyl ethylbenzoate were also prepared and their boiling points were found to be the same as reported by Claisen and Eisleb (*Annalen*, 1913, **401**, 82) and Anschutz *et al.* (*loc. cit.*).

*Esters of m-Cresotinic Acid.*—The two esters of *m*-cresotinic acid, 2-oxy-4-methyl methylbenzoate and 2-oxy-4-methyl ethylbenzoate, were obtained by Fischer's method by refluxing the acid with the requisite alcohol in presence of 3% hydrochloric acid gas. Their boiling points were in agreement with those reported by Biedermann (*Ber.*, 1873, **6**, 324) and Pinner (*loc. cit.*).

*Ether-esters of Cresotinic Acids.*—These compounds were obtained by refluxing for 4 hours, the sodium salt of the cresotinic acid-alkyl ester (1 mol.) with the required alkyl iodide (20% in excess) in absolute ethyl alcohol. The sodium salt was prepared by adding sodium (1 mol.) to excess of absolute alcohol and treating the sodium ethoxide, thus obtained, with the required ester (1 mol.). The excess of the alcohol was distilled off, the residual reaction mixture treated with water to dissolve the sodium iodide and extracted with ether. It was dehydrated over anhydrous sodium sulphate, the ether removed, and the residual liquid distilled under reduced pressure. The following ether-esters have been obtained.

TABLE II

Compounds, [B = benzoate]	B.p.	Yield.	Mol. formula.	C a r b o n		H y d r o g e n	
				Found.	Calc.	Found.	Calc.
(1) 2-Ethoxy 3-methyl methyl-B	154 /4 mm.	53.8%	C <sub>11</sub> H <sub>14</sub> O <sub>2</sub>	67.74%	68.04%	7.32%	7.22%
(2) 2-Methoxy 3-methyl ethyl-B	145°/25	51.6	C <sub>11</sub> H <sub>14</sub> O <sub>2</sub>	67.69	68.04	7.12	7.22
(3) 2-Ethoxy 3-methyl ethyl-B	148 /5	54.1	C <sub>12</sub> H <sub>16</sub> O <sub>2</sub>	68.84	69.23	7.58	7.69
(4) 2-Methoxy 3-methyl isopropyl B	135 /5	62.2	C <sub>12</sub> H <sub>16</sub> O <sub>2</sub>	68.93	69.23	7.44	7.69
(5) 2-Ethoxy 3-methyl isopropyl B	125 /5	43.7	C <sub>13</sub> H <sub>18</sub> O <sub>2</sub>	69.88	70.26	8.04	8.11
(6) 2-Methoxy 3-methyl <i>n</i> -butyl-B	162 /5	74.9	C <sub>13</sub> H <sub>18</sub> O <sub>2</sub>	69.94	70.26	8.06	8.11
(7) 2-Ethoxy 3-methyl <i>n</i> butyl B	168°/8	66.6	C <sub>14</sub> H <sub>20</sub> O <sub>2</sub>	70.96	71.16	8.41	8.47
(8) 2-Ethoxy 4-methyl methyl-B	140°/10	76.1	C <sub>11</sub> H <sub>14</sub> O <sub>2</sub>	67.92	68.04	7.14	7.22
(9) 2-Methoxy 4-methyl ethyl-B	152 /7	74.2	C <sub>11</sub> H <sub>14</sub> O <sub>2</sub>	67.88	68.04	7.26	7.22
(10) 2-Ethoxy 4-methyl ethyl-B	156 /5	86.5	C <sub>12</sub> H <sub>16</sub> O <sub>2</sub>	69.13	69.23	7.56	7.69

## STUDIES ON THE FRIES REARRANGEMENT. PART III

BY A. B. SEN AND V. S. MISRA

Several *o*-hydroxy-ketones have been prepared by the Fries rearrangement of esters of  $\alpha\beta$ -nonenoic acid.

The Fries rearrangement of esters of several unsaturated aliphatic acids has already been described in the first two parts of this series (Sen and Misra, this *Journal*, 1948, **25**, 393; 1949, **26**, 149). In all the three cases studied so far, only *o*-hydroxy-ketones were obtained. In the present paper this reaction has been extended to four esters of  $\alpha\beta$ -nonenoic acid, viz., phenyl, *o*-, *m*- and *p*-cresyl, which on treatment with anhydrous aluminium chloride have been found to rearrange mainly into *o*-hydroxy-ketones. The ketones have been characterised through their 2:4-dinitrophenylhydrazones.

### EXPERIMENTAL

*$\alpha\beta$ -Nonenoic acid* was prepared by the method described by Harding and Weizmann (*J. Chem. Soc.*, 1910, **97**, 301). Malonic acid (57 g.) was dissolved in dry pyridine (93 c.c.) and to the ice-cooled mixture was gradually added *n*-heptaldehyde (57 g.). The mixture was allowed to stand at the room temperature (28–32°) for 60 hours with frequent shaking, and finally heated on a water-bath for 6 hours. On acidification with 25% hydrochloric acid (200 c.c.), the  $\alpha\beta$ -nonenoic acid separated out as an oil. It was taken up in benzene, washed with water, dried and distilled under reduced pressure, b.p. 147°/7mm. (Harding and Weizmann, *loc. cit.* report b.p. 144°/13mm.), yield 65% of theory.

*Chloride of  $\alpha\beta$ -Nonenoic Acid*.— $\alpha\beta$ -Nonenoic acid (20 g.) and thionyl chloride (28 g.) were refluxed together for 4 hours on a water-bath. The excess of thionyl chloride was removed and the chloride distilled under reduced pressure, b.p. 104°/10mm. (Harding, *loc. cit.* reports b.p. 144°/90mm.).

*Phenyl Ester of  $\alpha\beta$ -Nonenoic Acid*.—To phenol (4.8 g.), taken in a round bottom flask fitted with a reflux condenser and a dropping funnel, was gradually added  $\alpha\beta$ -nonenoyl chloride (9 g.) and the mixture was heated on a water-bath till the evolution of hydrogen chloride had ceased. On cooling and addition of cold water, the ester separated out as an oil which was then extracted with ether, washed with water, 1% caustic soda and then again with water. The ethereal solution was dehydrated over anhydrous calcium chloride and the ether removed. The residue was distilled under reduced pressure when the ester was obtained as a colorless oil, b.p. 151°–152°/1mm., yield 10 g. (Found: C, 77.41; H, 8.43.  $C_{15}H_{20}O_2$  requires C, 77.58; H, 8.62 per cent).

**o*-Cresyl Ester of  $\alpha\beta$ -Nonenoic Acid*.— $\alpha\beta$ -Nonenoyl chloride (10 g.) was heated with freshly distilled *o*-cresol (6 g.) and the ester obtained in the usual manner, b.p. 176°/4mm., yield 10.5 g. (Found: C, 77.91; H, 8.81.  $C_{16}H_{22}O_2$  requires C, 78.04; H, 8.94 per cent).

*m*-Cresyl Ester of  $\alpha\beta$ -Nonenoic Acid.—To *m*-cresol (6 g.) was added  $\alpha\beta$ -nonenoyl chloride (10 g.) and the ester isolated as usual, b.p.  $167^{\circ}/4\text{mm.}$ , yield 9.5 g. (Found : C, 77.88 ; H, 8.65.  $\text{C}_{16}\text{H}_{22}\text{O}_2$  requires C, 78.04 ; H, 8.94 per cent).

*p*-Cresyl Ester of  $\alpha\beta$ -Nonenoic Acid.—The acid chloride (9 g.) was added to *p*-cresol (5.6 g.) and the ester isolated in the usual manner, b.p.  $181^{\circ}/3\text{mm.}$ , yield 9 g. (Found : C, 77.76 ; H, 9.05.  $\text{C}_{16}\text{H}_{22}\text{O}_2$  requires C, 78.04 ; H, 8.94 per cent).

*Fries Rearrangement of the Phenyl Ester of  $\alpha\beta$ -Nonenoic Acid.*—The ester (8 g.) was gradually added to finely powdered anhydrous aluminium chloride (6.8 g.) taken in a 250 c.c. round bottom flask, fitted with an upright condenser and a dropping funnel. The mixture was heated on a boiling water-bath for 2 hours and to the bluish red puffy mass obtained, dilute hydrochloric acid was added. A bluish oil separated out after some time, which was taken up in ether and washed successively with water, 1% sodium carbonate solution and finally with water. The ethereal extract was dehydrated over anhydrous sodium sulphate. After removal of the ether the residue was distilled under reduced pressure when a light blue oil was obtained at  $120^{\circ}/2\text{mm.}$ , yield 4.4 g. It conformed to the characteristic tests of *o*-hydroxy-ketones (Pyman, *J. Chem. Soc.*, 1930, 280) and was identified as 1-(2'-hydroxyphenyl)-non-2-ene-1-one. (Found : C, 77.32 ; H, 8.86.  $\text{C}_{15}\text{H}_{20}\text{O}_2$  requires C, 77.58 ; H, 8.62 per cent).

The 2:4-dinitrophenylhydrazone was obtained in the usual manner as red crystals, m.p.  $201^{\circ}$ . (Found : N, 13.78.  $\text{C}_{21}\text{H}_{21}\text{O}_5\text{N}_4$  requires N, 13.59 per cent).

1-(2'-Hydroxy-3'-methylphenyl)-non-2-ene-1-one. The above ketone was obtained by heating *o*-cresyl ester of  $\alpha\beta$ -nonenoic acid (8 g.) with anhydrous aluminium chloride (6.5 g.) and the *o*-hydroxy ketone isolated as in the preceding case, b.p.  $139^{\circ}/3\text{mm.}$ , yield 4.2 g. (Found : C, 78.26 ; H, 8.72.  $\text{C}_{16}\text{H}_{22}\text{O}_2$  requires C, 78.04 ; H, 8.94 per cent).

The 2:4-dinitrophenylhydrazone, obtained in the usual manner, melted at  $217-18^{\circ}$ . (Found : N, 12.84.  $\text{C}_{22}\text{H}_{26}\text{O}_5\text{N}_4$  requires N, 13.14 per cent).

1-(2'-Hydroxy-4'-methylphenyl)-non-2-ene-1-one.—The *m*-cresyl ester (9 g.) was heated with anhydrous aluminium chloride (7.2 g.) and the above ketone was obtained as a greenish oil, b.p.  $142^{\circ}/4\text{mm.}$ , yield 5 g. (Found : C, 78.36 ; H, 9.22.  $\text{C}_{16}\text{H}_{22}\text{O}_2$  requires C, 78.04, H, 8.94 per cent).

The 2:4-dinitrophenylhydrazone was obtained as before, m.p.  $221^{\circ}$ . (Found : N, 12.79.  $\text{C}_{22}\text{H}_{26}\text{O}_5\text{N}_4$  requires N, 13.14 per cent).

1-(2'-Hydroxy-5'-methylphenyl)-non-2-ene-1-one.—*p*-Cresyl ester (8 g.) on heating with anhydrous aluminium chloride (6.5 g.) gave exclusively the above ketone, b.p.  $132^{\circ}/4\text{mm.}$ , yield 4.9 g. (Found : C, 77.59 ; H, 9.42.  $\text{C}_{16}\text{H}_{22}\text{O}_2$  requires C, 78.04 ; H, 8.94 per cent).

The 2:4-dinitrophenylhydrazone was obtained as described previously, m.p.  $209^{\circ}$ . (Found : N, 13.33.  $\text{C}_{22}\text{H}_{26}\text{O}_5\text{N}_4$  requires N, 13.14 per cent).

## STUDIES ON THE FRIES REARRANGEMENT. PART IV

BY A. B. SEN AND V. S. MISRA

Fries rearrangement with esters of crotonic acid has been studied.

In a number of papers of this series (Sen and Misra, this *Journal*, 1948, **25**, 393, 1949, **26**, 149, 337) Fries rearrangement has been studied with esters of unsaturated aliphatic acids. In the present paper this reaction has been extended to esters of crotonic acid, which has a smaller number of carbon atoms than those already described. As in the previous cases, esters of phenol, *o*-, *m*- and *p*-cresols have been prepared. These esters on treatment with anhydrous aluminium chloride rearranged mainly into *ortho*-hydroxyketones (about 60-68%) which were characterised through their 2:4-dinitrophenylhydrazones.

It may be pointed out that acrylyl chloride on treatment with aluminium chloride in the presence of benzene is known to give 1-hydrindone (Kohler, *Amer. Chem. J.*, 1909, **42**, 375). In this case this possibility is ruled out as the product obtained gave the Baeyer's permanganate test and decolorised bromine in carbon tetrachloride, thus proving the presence of double bond in the molecule. Perhaps the presence of a methyl group in the  $\alpha$ -position inhibits the cyclisation to hydrindone.

The effect of temperature and solvent has also been studied with the *p*-cresyl ester of crotonic acid. The solvents used were chlorobenzene, nitrobenzene, tetrachloroethane and toluene and the temperature maintained at 100° except in the case of nitrobenzene (80°). The addition of solvent instead of improving the yields resulted in considerable lowering of yields and involved considerable experimental difficulty. From this study of effect of temperature the optimum condition arrived at for the rearrangement was found to be 140°, with 1.5 moles of anhydrous aluminium chloride and a reaction time of two hours.

### EXPERIMENTAL

*Crotonyl Chloride.* From crotonic acid (20 g.), suspended in 200 c.c. of petrol-ether, and 55 g. of thionyl chloride, 22 g. of crotonyl chloride were obtained by following the method of Staudinger *et al.* (*Ber.*, 1916, **49**, 1991), b.p. 123°-124° (Staudinger *et al.* report b.p. 124°-126°).

*Phenyl Ester of Crotonic Acid.*—To phenol (9.4 g.), taken in a 100 c.c. flask fitted with a reflux condenser and a dropping funnel, was gradually added crotonyl chloride (10.4 g.) and the mixture was heated on a water-bath for 2 hours. After cooling and addition of water the ester separated out as an oil which was taken up in ether, washed with 1% caustic soda and finally with water. The ethereal extract was dried over anhydrous sodium sulphate and the ether removed by distillation. The residual oil was distilled under reduced pressure, b.p. 161°/11mm., yield 11.5 g. (Found: C, 73.99; H, 6.21.  $C_{10}H_{10}O_2$  requires C, 74.07; H, 6.17 per cent).

*o*-Cresyl ester of crotonic acid was prepared as above from *o*-cresol (10.8 g.) and the acid chloride (10.4 g.), yield 10 g., b.p. 177°/11 mm. (Found : C, 75.12 ; H, 6.88.  $C_{11}H_{12}O_2$  requires C, 75.0; H, 6.81 per cent).

*m*-Cresyl ester of crotonic acid was prepared as above from 10.8 g. of *m*-cresol as light green oil, yield 10 g., b.p. 189°/10mm. (Found : C, 75.09 ; H, 6.87.  $C_{11}H_{12}O_2$  requires C, 75.0 ; H, 6.81 per cent).

*p*-Cresyl ester of crotonic acid was obtained as above from 10.8 g. of *p*-cresol, yield 11g., b.p. 181°/10mm. (Found : C 75.19 ; H, 6.92.  $C_{11}H_{12}O_2$  requires C, 75.0 ; H, 6.81 per cent).

#### Fries Rearrangement of the Esters

To finely powdered anhydrous aluminium chloride (0.48 *M*), taken in a 200 c.c. round bottom flask fitted with a reflux condenser and a dropping funnel, was gradually added 0.035*M* of the appropriate ester. The temperature of the external bath was raised to 140° and the mixture heated at this temperature for 2 hours. On cooling and addition of ice and dilute hydrochloric acid to the puffy mass, an oil separated out. It was taken up in ether, washed successively with water, 1% sodium carbonate solution and finally with water. After dehydration, the ether was removed and the residual oil distilled in vacuum. The distillate conformed to Pyman's test (*J. Chem. Soc.*, 1930, 280) for *o*-hydroxy-ketones.

These ketones thus obtained were all converted into the 2:4-dinitrophenylhydrazones which were recrystallised from hot toluene.

TABLE I

*Products of the Fries rearrangement of the above esters.*

<i>o</i> -Hydroxy-ketones.	B.p.	Dinitrophenylhydrazone M.p.	Mol. formula.	Nitrogen Found.	Nitrogen Calc.
(a)	140°/10 mm	169	$C_{16}H_{11}O_5N_4$	16.58%	16.37%
(b)	156°/11	174	$C_{17}H_{11}O_5N_4$	15.66	15.73
(c)	155°/10	167	$C_{17}H_{14}O_5N_4$	15.89	..
(d)	166°/10	178°	$C_{17}H_{16}O_5N_4$	15.45	..
(a) = 1-(2'-hydroxyphenyl)-but-2-en-1-one (Found: C, 73.62; H, 6.56. $C_{10}H_{10}O_2$ requires C, 74.07, H, 6.17%).					
(b) = 1-(2'-hydroxy-3'-methylphenyl)-but-2-en-1-one (Found: C, 74.58; H, 7.08. $C_{11}H_{12}O_2$ requires C, 75.0; H, 6.81%).					
(c) = 1-(2'-hydroxy-4'-methylphenyl)-but-2-en-1-one (Found: C, 74.68; H, 6.98. $C_{11}H_{12}O_2$ requires C, 75.0; H, 6.81%).					
(d) = 1-(2'-hydroxy-5'-methylphenyl)-but-2-en-1-one (Found: C, 74.86; H, 7.12. $C_{11}H_{12}O_2$ requires C, 75.0, H, 6.81%).					

**Temperature Effect.**—In all the following five experiments *para*-cresyl ester of crotonic acid (2g.) was added to finely powdered anhydrous aluminium chloride (2.4 g) and the reactions carried out at five different temperatures. Except in the case where the reaction tem-



perature was  $10^{\circ}$ , which was left for a week, the time employed was two hours. After the completion of the reaction the usual procedure, as described in the preceding page, was adopted, but the *o*-hydroxy-ketone instead of being distilled was isolated as a yellow crystalline sodium salt by the addition of dilute caustic soda to the ethereal solution. The crystalline derivative was filtered at the pump, washed with ether, and decomposed by dilute HCl when the *o*-hydroxy-ketone separated out as an oil. It was extracted with ether, the ethereal extract dehydrated over anhydrous sodium sulphate and the ether removed by evaporation. The residual oil was dried at  $100^{\circ}$  and subsequently weighed. The results are summarised in Table II.

TABLE II

Temperature.	Time.	Yield of the <i>o</i> -hydroxy-ketone
10	7 days	No effect only in traces
$100^{\circ}$	2 hours	0.3 g.
$120^{\circ}$	"	1.0 g.
140	"	1.3 g.
$165^{\circ}$	"	1.3 g. but accompanied with charring

*Solvent Effect*—In all four solvents, viz., nitrobenzene chlorobenzene, tetrachloroethane and toluene were employed. The amount of ester taken was 2 g. in every case and the time employed was two hours. Dry and freshly distilled solvent (7-8 c.c.) was added to finely powdered anhydrous aluminium chloride (2.4 g.) and the ester added to it. While using nitrobenzene as the solvent, the temperature employed was  $80^{\circ}$ , but in other three cases it was  $100^{\circ}$ . Lower temperatures were maintained because of the general observation that the use of solvents lowers the reaction temperature. After the completion of the reaction the usual method was adopted and the ketone was taken up in ether. The solvent used and the ether were removed by distillation at reduced pressure and to the residual oil dilute caustic soda was added. The yellow sodium derivative obtained was decomposed with dilute hydrochloric acid and the resulting oil taken up in ether, dried and the ether evaporated. The residual oil was dried at  $100^{\circ}$  and then weighed. The results are tabulated below.

TABLE III

Solvent.	Temperature.	Time.	Yield of the <i>o</i> -hydroxy-ketone.
Nitrobenzene	$80^{\circ}$	2 hours	0.43 g
Chlorobenzene	$100^{\circ}$	"	0.51
Tetrachloroethane	$100^{\circ}$	"	0.76
Toluene	$100^{\circ}$	"	0.61

# ESSENTIAL OIL FROM THE LEAVES OF *FERONIA ELEPHANTUM*, CORR.

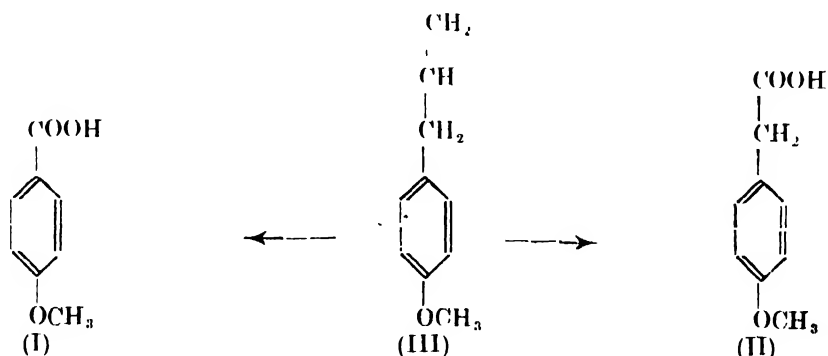
BY ASHA RAM BHATI AND S. S. DESHPANDE

The chief component of the essential oil from the leaves of Kavil (*F. elephantum*) is estragol which constitutes about 90% of the oil.

The tree is indigenous to S. India and Ceylon. Its leaves contain an essential oil which is said to be similar to that of the leaves from *Bel* (*Aegle marmelos*, Corr) ("Nadkarni, "Indian Materia Medica", p. 358), another member of the Rutaceae family. In continuation of our studies on the essential oil of *Bel* leaves (this *Journal*, 1939, 26, 231) the examination of the essential oil from wood apple or Elephant apple (Kavil in Hindi) leaves was thought to be of interest.

The leaves yield 0.73% oil, on steam distillation, of the following properties: boiling range, 209 to 211 (at atmospheric pressure);  $d_{25}^{20}$ , 0.9668;  $n_D^{25}$ , 1.5195;  $[\alpha]_D^{20}$ , 0°; saponification value, 11.0. It does not reduce Fehling's solution nor does it give any reaction characteristic of a carbonyl compound. The boiling range, optical inactivity and non-reducing properties indicate the absence of phellandrene (the chief component of the essential oil from *Bel* leaves) and the absence of aldehydes like citral or citronellal.

On refractionation, about 90% of the oil passes over between 210° and 212°. As repeated distillations do not alter the boiling range, this fraction has been taken to consist mostly of one individual compound. It has the molecular formula  $C_{10}H_{12}O$  and contains a methoxy group. It is unsaturated as is shown by the absorption of bromine in chloroform solution. On oxidation with hot neutral 4% potassium permanganate, anisic acid (I) is formed indicating the existence of a side chain in *para* position to the methoxy group and the double bond in the side chain. On milder oxidation with ice-cold 1% permanganate, *p*-methoxyphenylacetic acid (II) is produced. These properties indicate that the substance might be estragol (III)



The identity has been confirmed by preparing the nitrosite derivative by treatment

with amyl nitrite and hydrochloric acid and comparing with an authentic sample. These and other properties of our compound along with those of estragol are recorded below.

TABLE I

	The compound.	Estragol.
B. p.	210° to 212	214° (Klages, <i>Ber.</i> , 1899, <b>32</b> , 1439) 212 (Dupont & Guerlain, <i>Compt. rend.</i> , 1897, <b>124</b> , 300)
Density	0.9665 at 20	0.9645 at 21
$n_D$	1.5235	1.5236
$[\alpha]_D$	0°	0
M.p. of nitrosite	146°	147 (Rimm, <i>Gazzetta</i> , 1904, <b>34</b> , 284)
Oxidation with cold 1% $\text{KMnO}_4$	<i>p</i> -Methoxyphenyl acetic acid	<i>p</i> -Methoxyphenylacetic acid (Eijkman, <i>Ber.</i> , 1889, <b>22</b> , 2744)

## EXPERIMENTAL

The leaves (4 kilos) were distilled in steam in a copper still provided with a spiral copper condenser. The oil (14 c.c.) floating over the aqueous distillate was collected and from the aqueous layer 16 c.c. more were obtained by extraction with carbon tetrachloride. The total yield of the oil (14 + 16 = 30 c.c., 29 g.) was thus 0.73% of the weight of the leaves.

On repeated fractionation of the oil under atmospheric pressure the boiling range remained steady between 210° and 212°. The compound without further purification was analysed. [Found: C, 78.8; H, 8.1%; Me, 17.4; M.W., 142 (freezing point depression method in benzene solution).  $\text{C}_{10}\text{H}_{12}\text{O}$  requires C, 81.0; H, 8.0; Me, 20.90%. M.W., 148].

*Oxidation with 4% Permanganate.*—To the compound (3 g.) 4% neutral  $\text{KMnO}_4$  solution was added, first at room temperature and then at water-bath temperature until pink colour persisted. About 15 g. of permanganate were used up. On filtering, concentrating the filtrate and acidifying, a crystalline acid separated which crystallised from hot water in needles, m.p. 183°. The equivalent weight was determined by titration with 0.025*M* alkali. [Found: Equiv., 152.8.  $\text{C}_6\text{H}_5\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$  (m.p. 184°) requires equiv., 152].

*Oxidation with ice-cold 1% Permanganate.*—The compound was treated as described except that the temperature was kept throughout at 0°. An acid was obtained which crystallised from hot water in shining plates melting at 85–87°. [Found: Equiv., 166.9.  $\text{CH}_3\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{COOH}$  (m.p. 85–87°) requires equiv., 166].

*The Nitrosite.*—The usual method of preparing a nitrosite by the action of sodium nitrite, acetic acid and hydrochloric acid on an unsaturated compound gave a poor yield in the present case. After a number of trials the following method was found to give a satisfactory yield.

The liquid compound (2 c.c.) was dissolved in petroleum ether (4 c.c.) and the solution was cooled to ice temperature. Amyl nitrite (5 c.c.) and glacial acetic acid (6 c.c.) were then added and finally 10 drops of strong hydrochloric acid were added, the whole being maintained

at 0°. The mixture was then allowed to remain at room temperature for two days. The nitrosite, which separated as almost a colorless crystalline mass, was filtered at the pump and weighed (0.35 g.). The crude nitrosite melted at 134° but on repeated washing with dry ether the melting point rose to 146° and could not rise further. It was then analysed. (Found : C, 53.2, H, 5.4 ; N, 13.3.  $C_{10}H_{12}N_2O_4$  requires C, 53.5 ; N, 5.35 ; N, 12.5 per cent).

#### C O N C L U S I O N

Although Bel and Kavit both belong to Rutaceæ family the essential oils from their leaves differ completely from one another regarding their chemical composition. The chief component of the latter oil is estragol (methyl chavicol) which constitutes about 90% of the oil. Estragol occurs in small proportion in Russian aniseed oil and its best source so far has been estragon oil in which it occurs to the extent of 60% to 75%, the yield of the oil itself being 0.3% on the weight of the entire branches (Grimaux, *Bull. soc. chim.*, 1894, *in*, 11, 34). The leaves of Kavit is now the richest source for the compound.

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## ISOSTERIC HEATS OF ADSORPTION. PART I. ALCOHOLS ON SILICA GEL

BY B. P. GYANI

The heats of adsorption of methyl, ethyl, *n*-propyl, *sec*-propyl, and *n*-butyl alcohols on silica gel have been measured at different fixed concentrations. This has been done by observing the variation in equilibrium pressures of the systems with temperature.

It is well known that substances of the same chemical group usually show similarity in the process of adsorption in the sense that the adsorption isotherms have the same general shape and can be brought together by adopting a suitable mode of plotting the data. It is therefore expected that such compounds should also show a comparable temperature dependence, and hence possess heats of adsorption of the same order. The heats of adsorption of methyl alcohol and its nearest homologues on silica gel have been measured with an intention to see how far this expectation is fulfilled, and are described below.

Two different experimental procedures are open for investigating this matter. We may either measure the heat evolved when the adsorbent takes up successive small quantities of the vapour directly in a calorimeter, or we may determine the equilibrium pressures for the same fixed quantity of the adsorbate and adsorbent present, and obtain the heat by means of the thermodynamic relation for reaction at constant volume. On the experimental side, the first method presents difficulties due to slow attainment of equilibrium, bad conductivity of the materials, and so on. During adsorption neither the volume nor the pressure is quite constant, and hence the heat measured is thermodynamically ill-defined (Kruyt and Moddermann, *Chem. Rev.*, 1930, 7, 259). The choice of temperatures has often been limited and measurements have commonly been made by the ice-calorimeter. These disadvantages are mostly overcome in the tensimetric method adopted here. By this method the measurements may be carried out both at increasing and decreasing temperatures with equal ease and precision.

### EXPERIMENTAL

A tensimeter of simple design was constructed for these measurements. The form ultimately adopted is shown in Fig. 1. The adsorption bulb B containing some silica gel was sealed on to one limb of a U-tube manometer M. The gel was prevented from falling into the manometer, while handling the apparatus, by sealing in a small glass rod between the two constrictions at R. Another small bulb H was sealed on the other limb of M at about the same height as B. This side ended in a well ground glass tap T. Enough clean mercury was introduced into the manometer to fill about half the height on either side. The mercury was then collected in the bulb H by tilting the apparatus. The bulb was wrapped with a few folds of asbestos paper and heated with a small flame while the apparatus was being evacuated by means of a Cenco-Hyvac pump through T. When the evacuation was complete the tap T was closed and the bulb allowed to cool down. Some of the freshly distilled liquid under investigation was then introduced into the apparatus. The vapour was

rapidly taken up by the gel and the process was aided by cooling the bulb B. The excess liquid which condensed in B was heated to almost boiling and kept at that temperature for a few minutes to get rid of the adsorbed gases from the gel, not removed during evacuation. The excess was then pumped out, the tap T closed, and the mercury returned to the ma-

Fig. 1

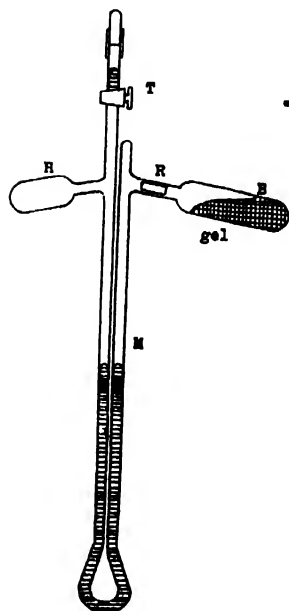
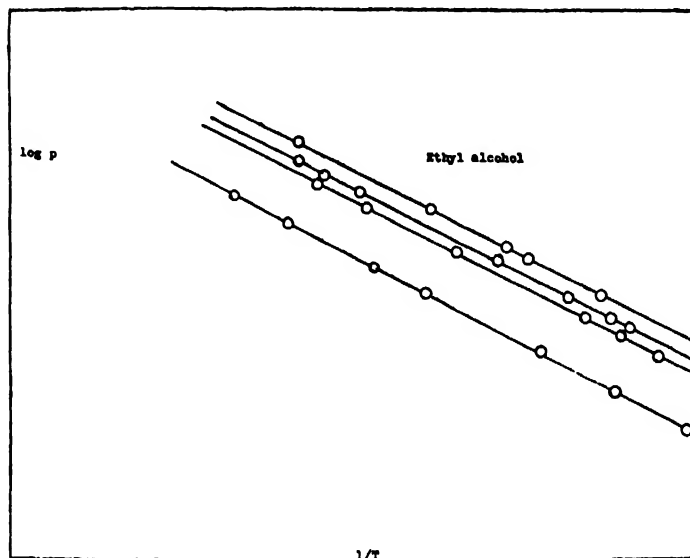


Fig. 2



nometer. The apparatus was then clamped vertically in a large air thermostat. The tap was sealed with a few drops of mercury and painted on the sides with molten Faraday cement. The thermostat was maintained at temperatures constant to within one-tenth of a degree. The temperature regulation was by means of a simple mercury-toluene thermoregulator working in conjunction with an electro-magnetic relay. The heater was joined across the spark-gap in series with a variable resistance so that a residual current was always kept flowing through it. This current was adjusted in the usual way to balance the loss of heat to the surroundings as closely as possible.

The pressure was read directly on a meter scale attached rigidly to the manometer, to fractions of a mm. This arrangement enabled readings to be taken up to a temperature of 65° without any difficulty. Above this temperature the cement sometimes gave way suddenly when the experiment had to be stopped. After reaching the highest temperatures, often above 70°, the temperature was gradually lowered and another set of observations was recorded. The two sets of data were always in good agreement with each other.

After completing runs at an arbitrarily fixed constant composition, the tensimeter was taken out of the thermostat. The mercury was again collected in H in order to pump out an amount of vapour and the apparatus was reset for another run at a lower composition. The value of the composition *i. e.*, the amount of liquid present in the gel, was computed by reference to a previously determined isotherm at 35°.

The silica gel employed in these experiments was prepared by the author by mixing together under vigorous shaking equal volumes of dilute solutions of commercial hydrochloric acid ( $d$  1.05) and sodium silicate (sp. gr. 1.12). The resulting sol required 3 to 4 hours to set to a stiff gel at the room temperature (about 30°). The raw gel was cut into pieces, washed free of electrolytes, and desiccated in gradual stages, finally in a current of dry air at 350°. The gel was a little opalescent. It was about two years old at the time of these measurements.

The measurements were performed with different quantities of the gel and some of them were checked up with a duplicate apparatus. One can therefore be sure that the results were not vitiated due to the presence of a small dead space inside the tensimeter, or non-uniformity of the gel.

The results of these observations are set down in the following tables. The first column gives the temperature  $T$  in degrees absolute, the second gives the pressure  $p$  in mm. of mercury. In the next two are recorded the values of  $\log_{10} p$  and  $1/T$  respectively. The next column shows the values of  $Q$ , the isosteric heat of adsorption, calculated as explained below. The pair of observations from which  $Q$  has been calculated is indicated in the sixth column.  $L$ , the latent heat of condensation of the vapour, is given at different temperatures where the vapour pressure data in the neighbourhood of that temperature are available in the literature

The van't Hoff expression for the heat of reaction at constant volume may be written as

$$\frac{d \log_{10} p}{d (1/T)} = \frac{Q}{2.303 \times R}$$

The value of the heat  $Q$  between any two temperatures  $T_1$  and  $T_2$  may be secured by taking the positive difference of the logs of the corresponding pressures  $p_1$  and  $p_2$  and dividing the result by the positive difference between  $1/T_1$  and  $1/T_2$ , then multiplying the quotient by  $2.303 \times R$ . Alternatively,  $\log p$  may be plotted against  $1/T$ . The slope of this curve is  $Q/2.303 \times R$  from which  $Q$  may be calculated. The mean value of  $Q$ , obtained by either of these methods, may be checked up by the centre of gravity method or the more exact method of least squares, since the relation between  $\log p$  and  $1/T$  is linear when  $Q$  is constant.

TABLE I

Ethyl alcohol  $87.20 \times 10^{-4}$  g. mol. per g. gel.

$T$ .	$p$ .	$\log p$ .	$1/T \times 10^3$ .	$Q$ calc. per mol.	$Q$ obtained from	$L$ calc. per mol
299.3	43.0 mm.	1.6335	3347	11680	1,2	10070
307.7	73.0	1.8633	3250	12110	2,3	10140
312.6	99.0	1.9956	3200	11530	3,4	10140
314.0	108	2.0334	3185	11700	4,5	10140
319.0	145	2.1614	3135	11200	5,6	10020
324.8	200	2.3010	3078	10650	6,7	9949
328.5	240	2.3802	3044	11000	5,7	9949

TABLE I (contd.)

Ethyl alcohol =  $83.28 \times 10^{-4}$  g. mol. per g. gel.

$T$ .	$p$ .	$\log p$ .	$1/T \times 10^4$ .	$Q$ calc. per mol.	$Q$ obtained from	$L$ calc. per mol.
304.5	56.0 mm.	1.7482	3284	11750	1,2	10140
313.8	100	2.0000	3186	11450	2,3	10020
320.7	148	2.1703	3118	11630	1,3	10020
312.6	93	1.9685	3200	11730	4,5	10140
315.8	113	2.0531	3167	11960	5,6	10020
318.0	129	2.1106	3145	10680	6,7	10020
324.4	181	2.2577	3082	11690	7,8	9949
326.7	206	2.3139	3060	10930	7,9	9949

Ethyl alcohol =  $72.13 \times 10^{-4}$  g. mol. per g. gel.

307.4	62.0	1.7924	3253	12280	1,2	10140
310.0	73.0	1.8633	3226	11820	2,3	10020
314.5	96.0	1.9823	3180	11050	3,4	9949
324.0	162	2.2095	3086	11840	4,5	9949
326.6	188	2.2742	3061	12110	5,6	9949
328.3	206	2.3139	3046	11930	4,6	9949
306.0	57.0	1.7559	3268	11130	1,7	10140

Ethyl alcohol =  $59.4 \times 10^{-4}$  g. mol. per g. gel.

304.3	46.0	1.6628	3286	13470	1,2	10140
306.7	54.5	1.7364	3261	11830	2,3	10140
308.8	62.5	1.7959	3238	11730	3,4	10140
317.4	104.5	1.0191	3151	10840	4,5	10020
323.5	145	1.1614	3091	10960	5,6	9949
327.0	174	1.2405	3058	10740	6,7	9949
329.5	197	1.2945	3035	10820	5,7	9949

Methyl alcohol =  $51.44 \times 10^{-4}$  g. mol. per g. gel.

316.0	13.0	2.1139	3165	9557	1,2	9200
323.1	18.2	2.2601	3095	9473	2,3	9200
326.3	211	2.3243	3064	11210	3,4	9200
329.1	243	2.3856	3039	10240	3,5	9200

Methyl alcohol =  $41.83 \times 10^{-4}$  g. mol. per g. gel.

303.0	42.0	1.6322	3300	9860	1,2	8976
312.5	69.9	1.8388	3200	10470	2,3	9221
321.5	108	2.0334	3115	10980	3,4	8904
325.5	137	2.1367	3072	10510	4,5	9215
329.2	164	2.2148	3038	10130	5,6	9215
330.7	177	2.2480	3023	10390	4,6	9215

Methyl alcohol =  $23.97 \times 10^{-4}$  g. mol. per g. gel.

303.5	5.5	0.7040	3284	12280	1,2	9221
310.7	8.8	0.9445	3219	11410	2,3	9221
316.7	12.0	1.0792	3165	12280	3,4	8904
322.2	17.5	1.2430	3104	11090	4,5	8904
326.4	22.0	1.3424	3060	13570	5,6	9215
329.7	27.0	1.4314	3033	11870	6,7	9215
334.2	34.5	1.5378	2992	12620	5,7	..

*n*-Propyl alcohol =  $59.55 \times 10^{-4}$  g. mol. per g. gel.

304.5	20.0	1.3010	3284	12630	1,2	11440
311.0	31.0	1.4814	3215	12620	2,3	11440
315.3	41.0	1.6128	3171	12840	3,4	11170
320.5	57.0	1.7559	3120	11710	4,5	11170
325.8	77.0	1.8865	3069	11850	5,6	10960
328.8	91.0	1.9591	3041	10720	6,7	10960
332.5	108.5	2.0364	3008	11710	7,8	10960
336.1	132.1	2.1209	2975	11670	6,8	10960



TABLE I (contd.)

*n*-Propyl alcohol— $55.0 \times 10^{-1}$  g. mol. per g. gel.

<i>T</i> .	<i>p</i> .	log <i>p</i> .	$1/T \times 10^3$	<i>Q</i> calc. per mol.	<i>Q</i> obtained from	<i>L</i> calc. per mol.
305.1	15.0 mm.	1.1761	3278	12280	1,2	11440
342.2	27.0	1.1314	3183	12780	2,4	11170
314.7	28.2	1.4502	3178	13300	3,5	11170
319.3	37.5	1.5740	3132	12840	4,5	11170
326.4	58.5	1.7672	3063	12700	5,6	10960
331.0	76.5	1.8837	3021	12770	4,6	10960

*sec*-Propyl alcohol— $27.24 \times 10^{-1}$  g. mol. per g. gel.

307.5	11.5	1.0607	3252	13620	1,2	
313.0	17.0	1.2304	3195	13210	2,3	
318.8	25.0	1.3979	3137	12580	3,4	
322.8	32.0	1.5051	3098	13760	4,5	
328.5	46.5	1.6675	3044	13550	5,6	
333.0	61.5	1.7889	3003	13670	4,6	

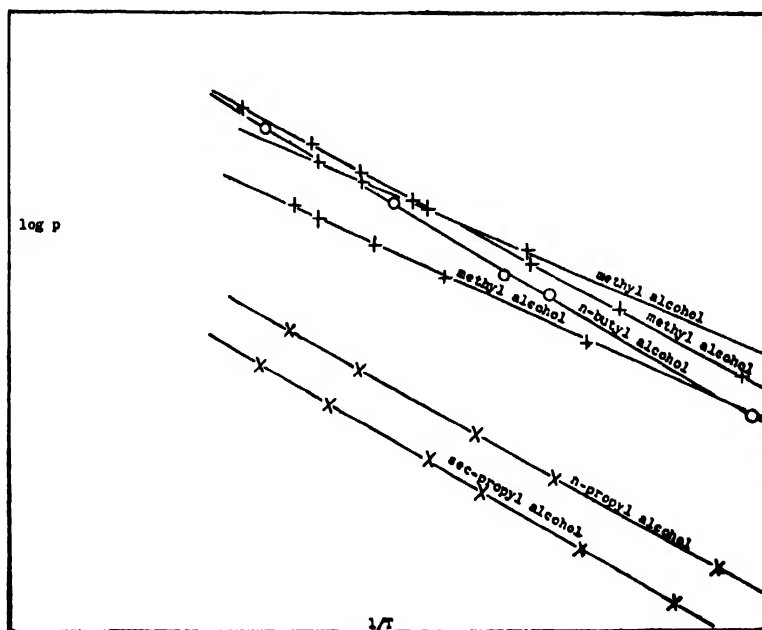
*n*-Butyl alcohol— $11.48 \times 10^{-1}$  g. mol. per g. gel.

310.5	9.5	0.9823	3138	13710	1,2	
317.4	11.0	1.0414	3151	14940	2,3	
324.2	18.2	1.2601	3084	13300	3,4	
332.5	31.0	1.4914	3008	14230	2,4	

## DISCUSSION

The values of log *p* have been plotted against  $1/T$  in Figs. 2 and 3. It will be seen that

FIG. 3



the graphs are all rectilinear and the individual points rarely show any notable deviations. This means that there is no temperature variation of *Q*. This point is further discussed below.

*Variation of Q with increasing Molecular Weight*

The average values of  $Q$  for the various compounds at different concentrations are summarised in the following table. The figure under every compound gives its dipole moment in the usual units.

TABLE II

Substance.	$x/m$ (g. mol. $\times 10^{-4}$ )	Average $Q$ , (cal./mol.).	Substance.	$x/m$ (g. mol. $\times 10^{-4}$ )	Average $Q$ (cal./mol.).
Methyl alcohol 1.73	51.44	9223	<i>n</i> -Propyl alcohol 1.65	59.55	12620
	41.83	9826		55.00	12778
	23.97	11470	<i>sec</i> -Propyl alcohol	27.24	13230
Ethyl alcohol 1.72	87.00	11520	<i>n</i> -Butyl alcohol 1.65	41.48	13970
	83.28	11570			
	72.13	11450			
	59.74	11530			
	40.80	11920			

Some general conclusions may be drawn from a study of this table. In the series of alcohols the heat of adsorption at comparable concentrations increases as the molecular weight is increased. The heat does not change much with increasing amount of adsorption but there is a general tendency for it to decrease as the concentration increases. In the case of ethyl alcohol, for example,  $Q$  is practically constant over a range of concentrations of about 60 to 87 g. mol.  $\times 10^{-4}$  per g. of the gel. Data for the *n*- and *sec*-propyl alcohols were unfortunately not obtained at comparable concentrations, but it seems safe to conclude that the branching chain has no effect on  $Q$  when we take into account the increase in its value due to falling concentration.

*Variation with Dipole Moment and Temperature*

As far as these alcohols are concerned we note that the dipole moment decreases as the molecular weight is increased, but at the same time  $Q$  has a tendency to increase. The permanent dipole moment of the adsorbed molecules should therefore be considered as relatively unimportant in bringing about the attachment resulting in adsorption as far as the present systems are concerned. However, the permanent dipole moment is not the only important factor in physical attachment. The group of forces known as van der Waals forces collectively is made up of other forces also which may be equally or more important. Thus, in the case of two non-polar molecules, the total van der Waals interaction energy is given by

$$U = U_{\text{repulsion}} + U_{\text{dispersion}} + U_{\text{quadrupole}}$$

If the molecules in addition possess permanent dipoles, two new terms corresponding to their orientation and the induction produced by them would appear. None of these energy terms is directly dependent on temperature. It is therefore understandable that the measured values of  $Q$  show little variation with temperature.

The equation of Magnus (*Z. physikal. Chem.*, 1929, **141A**, 270) for the heat of adsorption of a dipole or a quadrupole on a conducting surface is

$$\frac{q_0}{R} = c_k - (2/3) mT$$

where  $q_0$  is the constant heat of adsorption in the beginning portion of the isotherm,  $R$ , the gas constant, and  $c_k$  and  $m$  are constants typical of the adsorbed molecule. Though silica gel is not a conductor, Kälbere and Schuster's measurements (*Z. physikal. Chem.*, 1929, **142A**, 270) of the heat of adsorption of  $\text{CO}_2$  on it are found to be in agreement with this equation. The present measurements often extend to a temperature range of  $40^\circ$  but the decrease in the value of  $Q$ , demanded by this equation, has not been noted in a single case. The decrease in the above cited case was about 25% of the total heat of adsorption and about 10% for the adsorption of water by charcoal, the increase in temperature being  $40^\circ$ . The present results are in agreement with most of the previous ones obtained by others with organic vapours on charcoal in this respect (Lamb and Coolidge and Pearce *et al.*, *vide infra*). The constancy of  $Q$  is remarkable in view of the fact that the latent heat of vaporisation decreases appreciably as the temperature is increased (see tables above).

#### *Comparison with the Charcoal Data*

The values of the heats of adsorption of organic vapours on charcoal, as obtained by Lamb and Coolidge (*J. Amer. Chem. Soc.*, 1920, **42**, 1146) in an ice calorimeter are higher than those obtained in the present experiments in which the adsorbent is silica gel. The calorimetric and tensimetric measurements in general do not give identical results and the calorimetric values are as a rule higher, as shown by Pearce and his collaborators (*J. Phys. Chem.*, 1930, **34**, 1260; 1931, **35** 1091; 1935, **39**, 293). The values of Lamb and Coolidge correspond to a concentration of about  $20 \times 10^{-4}$  g. mol per g. of the charcoal and are contained in the following table.

TABLE III

Substance.	Present work.		Lamb & Coolidge.	
	Conc.	$Q$ (tensimetric)	Conc.	$Q$ (calorimetric)
Methyl alcohol	23.97	11470	20.0	13100
Ethyl alcohol	40.80	11920	20.0	15000

The present values of  $Q$  are clearly smaller than those of Lamb and Coolidge, but in view of the fact that the tensimetric method gives smaller values, one may conclude that each of the two alcohols on the two adsorbents has more or less equal values of  $Q$ . Evidently the equality will improve if the concentrations for the present values are reduced to be comparable with those of Lamb and Coolidge. One should also note that the measurements of these workers refer to a temperature of  $0^\circ$ , at which the vapours have a larger tendency to condense to a liquid. The whole matter merits further investigation.

#### *Comparison with the Latent Heat of Condensation*

One can see from Table I that the total heat of adsorption  $Q$  is always larger than  $L$ , the heat of condensation of the vapour to a liquid in bulk. Thus, the quantity  $Q-L$  which has been called the net heat of adsorption (*J. Amer. Chem. Soc.*, 1920, **42**, 1146) is always positive. The excess of  $Q$  over  $L$  can be explained if one assumes that the liquid in the adsor-

bed state is under compression. This postulate militates directly against the Kelvin equation or more directly the fundamental equation of capillarity

$$P = \sigma(1/R_1 + 1/R_2)$$

which requires that the liquid should exist under tension.

The net heat of adsorption is not always constant for different concentrations of the adsorbate except when the gel is fairly saturated. Even then the net heat is appreciable. Thus, it amounts to about 15% of the total  $Q$  for ethyl alcohol when  $x/m$  is in the range of 72 to 87 g. mol.  $\times 10^{-4}$  per g. of the gel. For other alcohols it amounts to less than 10% at higher concentrations. At lower concentrations, the value shows a definite increase. It is 25% of the total  $Q$  when the gel has 60 and 24 units of  $x/m$  for ethyl and methyl alcohols respectively. The net heats of adsorption for carbon tetrachloride and chloroform are low, about 10% of the total  $Q$ , and almost constant as will be shown in a subsequent communication.

Although  $Q$  is always larger than  $L$ , one has to note that the two quantities are always of the same order of magnitude. The heat of reaction of some processes such as hydration of inorganic and organic materials, which is definitely chemical in nature, is also of the same order as has been pointed out by McBain ("Sorption of Gases and Vapours", p. 410, George Routledge and Sons, London, 1932). Condensation and hydration may be regarded as examples of purely physical and chemical processes respectively. The heat changes accompanying them "resemble corresponding values for sorption so strikingly that it is evident that all the reactions involved refer to generalisations which are wider than the scope of any purely physical or chemical conceptions. Stress cannot be laid upon a particular success in explaining data according to one special hypothesis without consideration of the whole general subject of chemical and physical interaction."

The author is grateful to Lt. Col. Sir C. P. N. Singh for his kind interest in this work. The author also thanks Professors S. Sugden and P. B. Ganguly for their many valuable criticisms.

## DURABILITY OF SODA—LIME—SILICATE GLASSES. PART II

BY ARUP KUMAR BOSE, AMALENDRA CHOWDHURY AND H. N. DAS-GUPTA

The effect of composition on the durability of glass has been studied. It has been shown that two or more glasses of different compositions can possess identical durability. The possibility of theoretically calculating the durability of a glass (in terms of  $H_2SO_4$  value) from a knowledge of its composition has been attempted.

In a previous communication (Chowdhury and Das-Gupta, this *Journal*, 1947, **24**, 477), a study of the effect of substitution of known amounts of a given constituent upon durabilities of a series of 'like' glasses was made. The relation between chemical durability and composition of different series of 'like' glasses was also represented graphically, and the method of representing such a relation was illustrated there. Those curves indicate the possibility of obtaining identical durability for a number of glass compositions. This aspect of the problem was partly verified experimentally. The present paper embraces the following:

- (1) Further study of the effect of composition on durability.
- (2) To establish finally our finding that two or more glasses of different compositions can possess identical durability.
- (3) To explore the possibility of calculating, theoretically, the durability of a glass (expressed in terms of sulphuric acid value) from a knowledge of its composition.

Gelstharp and Parkinson (*Trans. Amer. Cer. Soc.*, 1914, **16**, 109) had made a systematic study in respect of compositions suitable for proper soda-lime-silicate glasses and they had represented their data by a tri-axial diagram. With a view to studying further the relation between composition and durability, the compositions have been so selected that they are well within the range specified for transparent glass proper, including technical glass. The durabilities of glasses produced were determined by 'Powder test' (Faraday, *Phil. Trans.*, 1830, p.49; Pelouze, *Compt. rend.*, 1856, **43**, 117; Mylius and Foerster, *Ber.*, 1889, **22**, 1092; *Z. Instrum. Kunde*, 1889, **9**, 120; Hagmaier, *Met. Chem. Eng.*, 1917, **16**, 604; Nicolardot, *Compt. rend.*, 1919, **169**, 335; Peddle, *J. Soc. Glass Tech.*, 1920, **4**, 3, 299; 1921, **5**, 72, 195).

The relation between composition and durability of different 'like' glasses (including those in Table III, part I) has been shown in Fig.1. In order to establish our second object, compositions, corresponding to different sulphuric acid values, have been computed from the curves of Fig.1. Table V shows such computed compositions and the sulphuric acid values actually found out.

The curves of Fig.1 may be utilised to draw contour lines. Thus, if the set of compositions, corresponding to a particular acid value, be plotted in the phase equilibrium diagram of the ternary system  $Na_2O-CaO-SiO_2$  after Morey and Bowen (*J. Soc. Glass Tech.*, 1925, **9**, 226), these will be represented by several points. A line joining these points would represent compositions having the same sulphuric acid value. Similarly, for different sets corresponding lines may be drawn. From analogy with iso-property curves or 'contour' lines like isotherms (Morey and Bowen, *loc. cit.*), and Isokoms (Washburn, Shelton and Libman,

Univ. Ill. Eng. Expt. Station Bull., 1924, p.140), these curves (Fig.2) have been designated as iso-durability curves.

It is well known that some of the physical properties of glass are additive in character. No serious attempt has been made with a view to correlating chemical durability of glass, in terms of sulphuric acid value, with its composition except, however, by empirical formulæ. It appears that Lyle, Horak and Sharp (*J. Amer. Cer. Soc.*, 1936, **19**, 142) made a study of the effect of alumina on chemical durability of glass. The results obtained with glasses containing  $\text{Na}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  were represented by the formula :

$\log D = 6.427 + 5.89 \log (N+A) - 0.654 (\log A)$ , in which D represents the durability in terms of the number of c.c. of  $0.02N\text{-H}_2\text{SO}_4$  required to neutralise the alkali extracted from 10g. of glass, and N and A represent the percentages of  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  respectively. This formula, however, gives the maximum effect in respect of durability. As stated earlier, the chemical durability of glass is a function of the percentages of the different constituent oxides, and as such, there can be no reason why these cannot be linked up theoretically. Thus, from analogy with other physical properties, this relation may be represented roughly by means of a formula of the type :

$D = aX + bY + cZ$ , in which D represents durability in terms of sulphuric acid value and X, Y and Z represent the percentages of  $\text{SiO}_2$ ,  $\text{CaO}$  and  $\text{Na}_2\text{O}$  respectively and 'a', 'b' and 'c' represent the corresponding factors. The values for the factors 'a', 'b' and 'c' have been worked out by solving different sets of three equations of each and taking the mean values. These equations are framed by substituting the actual values of D, X, Y and Z from Table IV. It will be seen that the calculated values for 'a' and 'b' are negative. This supports the fact that silica and lime impart increased durability in glass. Also, the value for 'b' is more negative than that for 'a', and this is in agreement with the observation that substitution of silica by a diabasic oxide, the alkali remaining constant, improves durability (Enss, *Glastech. Ber.*, 1928, **5**, 1). The values for 'c' is highly positive and this should naturally be the case.

#### EXPERIMENTAL

The procedure adopted for melting, plaining, and annealing the glasses of different compositions was the same as on the previous occasion (Part I, *loc. cit.*). Five series of glass batches were melted, and as usual, the percentage of silica in each series was kept constant, while successive amounts of  $\text{Na}_2\text{O}$  were replaced by lime. The sources of raw materials for glasses were different. Table I shows the purity of raw materials used and Table II gives the compositions of the glasses melted.

TABLE I

Material.	Percentage of						
	$\text{SiO}_2$ .	$\text{Fe}_2\text{O}_3$ .	$\text{Al}_2\text{O}_3$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{Na}_2\text{CO}_3$ .	Loss.
Sand (Series D & E)	97.96	Trace	1.59	—	—	—	0.47
„ (rest)	97.44	0.51	1.24	0.32	—	—	0.46
Lime (Series D & E)	1.39	2.04	0.30	69.87	Trace	—	26.30
„ (rest)	2.01	0.41	4.90	71.51	Trace	—	20.98
Heavy soda-ash (D & E)	—	—	—	S. trace	S. trace	90.87	9.05
„ (rest)	0.35	—	—	0.08	S. trace	90.85	8.60

TABLE II

Batch No.	Batch mixture (in g.)		Percentage composition				Remarks.
	Sand.	Soda.	Lime.	SiO <sub>2</sub> .	Na <sub>2</sub> O.	CaO.	
Series B <sub>1</sub>							
22	71.83	22.58	25.21	70	12	18	Clear, slight scum
23	71.83	24.46	23.80	70	13	17	Do
24	71.83	26.34	22.41	70	14	16	Very clear melt
25	71.83	28.23	20.98	70	15	15	Do
Series D							
26	76.56	28.32	14.31	75	15	10	Slight devitrification
27	76.56	23.50	17.89	75	12.5	12.5	Do
Series E							
28	69.41	37.63	17.17	68	20	12	Bright melt
29	69.41	33.87	20.03	68	18	14	Do
30	69.41	31.79	23.61	68	15.5	16.5	Clear melt
31	69.41	29.73	25.04	68	14.5	17.5	Do
32	69.41	24.46	27.19	68	13	19	Do
33	69.41	22.60	28.62	68	12	20	Scum formation
34	69.41	18.81	31.46	68	10	22	Thick scum with stone formation.
Series E <sub>1</sub>							
35	69.86	26.34	25.21	68	14	18	Clear melt
36	69.86	28.23	23.80	68	15	17	Very clear melt
37	69.86	30.10	22.41	68	16	16	Do
38	69.86	31.98	20.98	68	17	15	Do
Series F							
39	67.81	26.34	27.98	66	14	20	Perfectly clear
40	67.81	28.23	26.56	66	15	19	Do
41	67.81	30.1	25.21	66	16	18	Do
42	67.81	31.98	23.80	66	17	17	Do

It may be pointed out that in Table II minute traces of silica, lime, etc., derived from sources other than specified, have not been taken into account.

Ordinarily, during founding of glass, the composition varies to some extent. The extent of such variation will be clear from Table III, showing complete analyses of the three different samples.

TABLE III

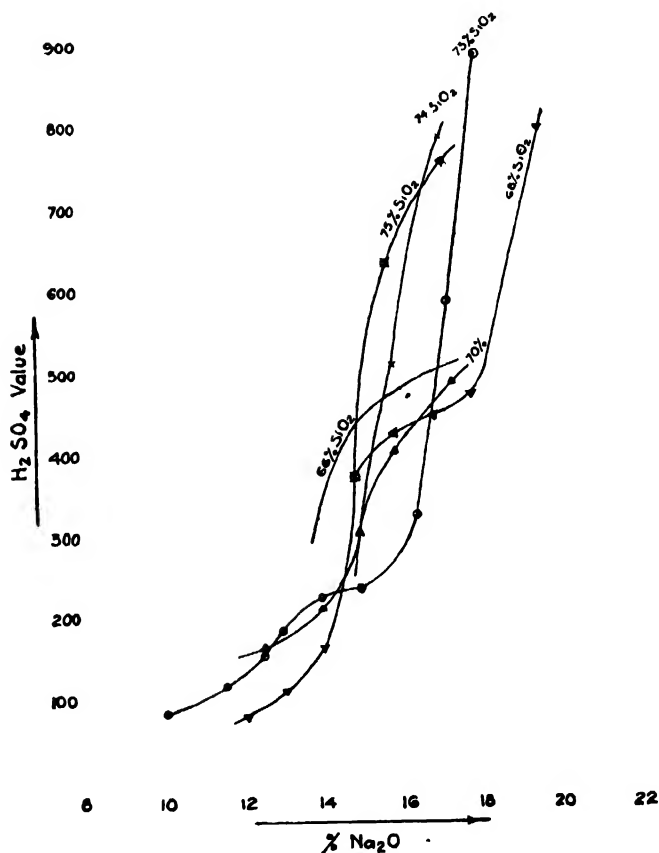
Sample.	Percentage composition expected					Percentage composition found]				
	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	Na <sub>2</sub> O.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	Na <sub>2</sub> O.
1.	68.23	2.05	0.46	17.65	11.61	68.63	2.2	0.52	17.41	11.12
2.	66.43	1.96	0.43	15.71	15.47	66.87	2.24	0.46	15.65	14.7
3.	64.49	1.93	0.42	16.69	16.47	65.06	2.00	0.50	16.49	15.9

The results of powder test have been incorporated in Table IV and the graphic relation has been shown in Fig. 1. As mentioned before, Fig. 2 shows similar relation for all glasses, inclusive of those included in Table III, Part I (*loc. cit.*).

### TABLE IV

Batch No.	H <sub>2</sub> SO <sub>4</sub> value.	Batch No.	H <sub>2</sub> SO <sub>4</sub> value.	Batch No.	H <sub>2</sub> SO <sub>4</sub> value.
	Series B <sub>1</sub> .		Series E.		Series E <sub>1</sub> .
22	160	28	800	35	161.4
23	181.9	29	465	36	371.6
24	218.1	30	400	37	415.7
25	299.2	32	112	38	436.2
		33	82		
	Series D				Series F.
26	368			39	321.7
27	156			40	428.8
				41	470.9
				42	496.1

Fig 1



From Fig. 1 several compositions corresponding to different sulphuric acid values have been computed. The results of powder test, made in respect of these glasses, have been incorporated in Table V. It will be seen that the experimental values are in close agreement with the expected values. This establishes our finding regarding the possibility of preparing iso-durable glasses.

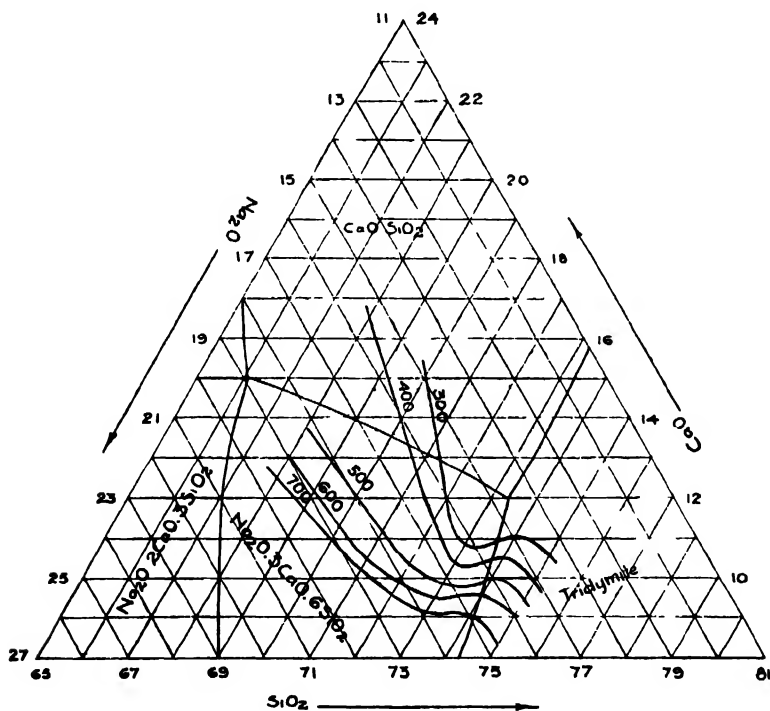


TABLE V

Computed compositions(%)			Sulphuric acid value.	
SiO <sub>2</sub> .	Na <sub>2</sub> O.	CaO.	Expected.	Found.
70	13.5	17.5	200	196.0
73	13.25	13.75	200	198.2
74	14	12	200	196.5
70	15	15	300	303
73	16.3	10.7	300	308
74	15	11	300	290
75	14.5	10.5	300	310
73	17.2	9.8	500	510
74	16	10	500	506
75	15.6	9.4	500	503

As explained earlier, Fig. 1 also furnishes the possibility of computing compositions for iso-durable curves. These points have been plotted in the phase equilibrium diagram of the ternary system, Na<sub>2</sub>O—CaO—SiO<sub>2</sub>, after Morey and Bowen (*loc. cit.*) and Fig. 2 shows the actual dispositions of these curves.,

Fig. 2



The question of linking up theoretically the durability of a glass with its composition has been but approximately solved. The calculated values agree with the expected values within certain range and up to a maximum of 15% Na<sub>2</sub>O in the glass. In the formula,  $D = aX + bY + cZ$ , the influences of traces of MgO, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, etc., have not been taken into account. This may be the reason why in almost every case the calculated

figure is higher than the actual values. If, however, the alkali content exceeds 15%, there is appreciable divergence between the calculated and the observed values. The worked out values for the factors 'a', 'b' and 'c', are respectively as -0.8, -9 and +30. Table VI embraces a few glass compositions, showing calculated and observed sulphuric acid values.

TABLE VI

SiO <sub>2</sub>	% Composition		Sulphuric acid value	
	CaO.	Na <sub>2</sub> O	Observed.	Calculated. (a = -0.8, b = -9 & c = 30)
73	12	15	235	283
73	13	14	225	249
73	14	13	186	205
73	14.5	12.5	154	187.1
73	15.5	11.5	119	147
73	17	10	93	98
73	10.5	16.5	320	357.5
73	9.5	17.5	578	381
73	8.5	18.5	879	320
70	12.5	17.5	479	357
70	14	16	399	298
70	15	15	303	259
70	17.5	12.5	164	162
70	16	14	218	220
74	8.5	17.5	783	389
74	10	16	506	331
74	11	15	290	292
74	13.5	12.5	156	194.3

The authors' grateful thanks are due to Mr. N. C. Nag, Chief Chemist and Director and to Mr. N. G. Sirkar, Works Manager & Director, Messrs. Sigcol & Co., Calcutta, for the supply of raw materials.

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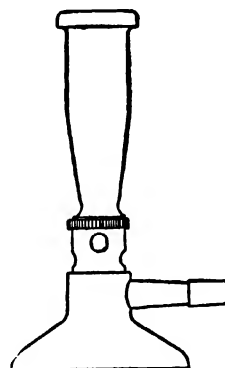
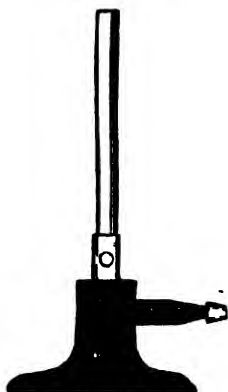
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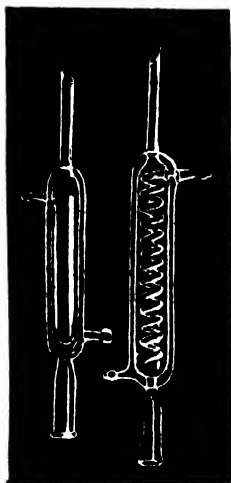
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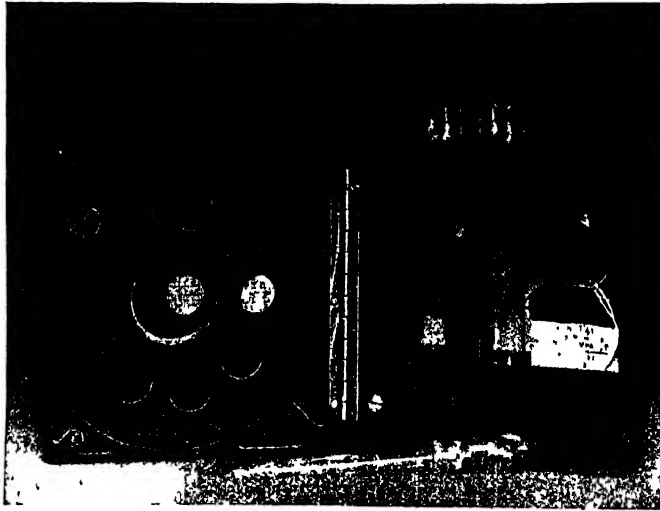
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# BROMINATION OF COUMARINS. PART I. BROMINATION OF 7-HYDROXY-4-METHYLCOUMARIN, METHYL 7-HYDROXY-4-METHYLCOUMARIN-6-CARBOXYLATE, 7-HYDROXY-4-METHYLCOUMARIN-6-CARBOXYLIC ACID AND THEIR METHYL ETHERS

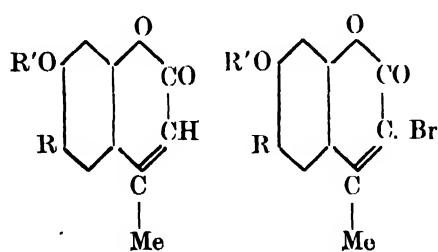
BY VIJAY JAYWANT DALVI AND SURESH SETHNA

7-Hydroxy-4-methylcoumarin, 7-hydroxy-4-methylcoumarin-6-carboxylic acid, methyl 7-hydroxy-4-methylcoumarin-6-carboxylate and their methyl ethers have been brominated with one molecule, two molecules and excess of bromine. It has been found that the first bromine atom in all cases enters the 3-position and the subsequent bromine atoms enter the benzene ring.

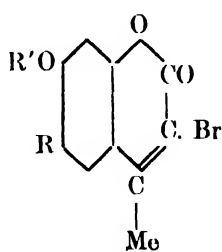
In the case of 7-hydroxy-4-methylcoumarin both the 3:6- and the 3:8-dibromocoumarins are obtained, the former being in preponderating yield. In the bromination of the 7-methoxy-4-methylcoumarin only the 3:6-dibromo derivative is formed, thus indicating that the 6-position is more reactive than the 8-position. Both the 3:6- and the 3:8-dibromo derivatives give the same 3:6:8-tribromo derivative on further bromination.

In the bromination of the hydroxy-ester, the hydroxy-acid and their methyl ethers, bromination with one molecule proceeds smoothly, the bromine atom entering the 3-position. The second bromine atom enters the 8-position but with difficulty. No dibromo product has been obtained in the direct bromination of the methoxy ester and the methoxy-acid.

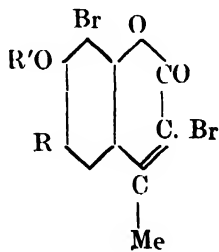
In the bromination of coumarins it has been found by various workers that generally the first bromine atom enters the 3-position and the subsequent bromine atoms enter the benzene nucleus. It has been found, however, by Dey and Kutti (*Proc. Nat. Inst. Sci. India*, 1940, **6**, 641) that in the bromination of 8-methoxycoumarin the first bromine atom enters the 5-position. Further, Fries and Lindemann (*Annalen*, 1914, **404**, 53) have assigned the structure of 7-hydroxy-8-bromo-4-methylcoumarin to the product obtained on bromination of 7-hydroxy-4-methylcoumarin, since it was found to be different from 7-hydroxy-6-bromo-4-methylcoumarin obtained by the Pechmann condensation of 4-bromoresorcinol with ethyl acetoacetate. In view of these results it was thought of interest to study the bromination of various coumarin derivatives, (i) to ascertain the reactivity of the different positions and (ii) to study the effect of substituents in the coumarin ring system on the course of bromination.



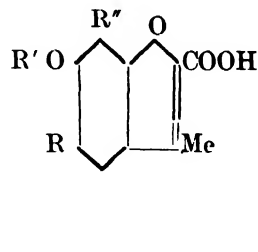
(I)



(II)



(III)



(IV)

7-Hydroxy-4-methylcoumarin (I,  $R=R'=H$ ) on bromination with one molecule of bromine gave the 3-bromocoumarin (II,  $R=R'=H$ ), previously obtained by Fries and Nohren (*Ber.*, 1935, **58B**, 1027) by bromination of the ethyl carbonate of 7-hydroxy-4-methylcoumarin and subsequent hydrolysis of the bromo compound with alcoholic ammonium hydroxide to get the free hydroxy compound. Its methyl ether was found to be identical, on direct comparison, with 7-methoxy-3-bromo-4-methylcoumarin (II,  $R=H$ ,  $R'=Me$ ) obtained from the methyl ether of (I,  $R=R'=H$ ) by bromination. The bromo compound has been previously obtained similarly by Limaye and Bhide (*Rasayanam*, 1938, **1**, 136). Thus, the structure of 7-hydroxy-8-bromo-4-methylcoumarin assigned to the bromination product of 7-hydroxy-4-methylcoumarin by Fries and Lindemann (*loc. cit.*) is found to be incorrect.

On bromination with two molecules of bromine, I ( $R=R'=H$ ) gave a mixture of the 3:6-dibromo-(II,  $R=Br$ ,  $R'=H$ ) and the 3:8-dibromocoumarin (III,  $R=R'=H$ ). The methyl ethers were prepared and on hydrolysis they gave bromocoumarilic acid derivatives (IV,  $R=Br$ ,  $R'=Me$ ,  $R''=H$  and IV,  $R=H$ ,  $R'=Me$ ,  $R''=Br$  respectively), thus indicating that one bromine atom in both the compounds is in the 3-position. One of the methyl ethers was found to be identical with the only dibromo compound obtained in the bromination of 7-methoxy-4-methylcoumarin with two molecules of bromine. The structure of 7-methoxy-3:6-dibromo-4-methylcoumarin (II,  $R=Br$ ,  $R'=Me$ ) was assigned to this product because it was found to be identical with the dibromo compound obtained on bromination of 7-methoxy-6-bromo-4-methylcoumarin which was prepared according to Chakravarti and Mukerjee (*J. Indian Chem. Soc.*, 1937, **14**, 725) from 4-bromoresorcinol. The other compound was therefore 7-methoxy-3:8-dibromo-4-methylcoumarin (III,  $R=H$ ,  $R'=Me$ ). 7-Methoxy-3:6-dibromo-4-methylcoumarin has been previously obtained by Limaye and Bhide (*loc. cit.*) but they did not assign a definite constitution to this product.

The coumarin I ( $R=R'=H$ ) with excess of liquid bromine gave the 3:6:8-tribromo compound (III,  $R=Br$ ,  $R'=H$ ). The methyl ether of this was found to be identical with the 3:6:8-tribromocoumarin (III,  $R=Br$ ,  $R'=Me$ ) obtained by the bromination of the methyl ether of I ( $R=R'=H$ ).

Methyl 7-hydroxy-4-methylcoumarin-6-carboxylate (I,  $R=CO_2Me$ ,  $R'=H$ ), prepared according to Shah *et al.* (*J. Indian Chem. Soc.*, 1937, **14**, 717), on bromination with one molecule of bromine gave the 3-bromocoumarin (II,  $R=CO_2Me$ ,  $R'=H$ ). Its methyl ether was found to be identical with the bromocoumarin obtained by the bromination of the methyl ether of I ( $R=CO_2Me$ ,  $R'=H$ ) with one molecule of bromine.

7-Hydroxy-4-methylcoumarin-6-carboxylic acid (I,  $R=CO_2H$ ,  $R'=H$ ) (Shah *et al.*, *loc. cit.*) on bromination with one molecule of bromine gave the 3-bromo-acid, identical with the product obtained on hydrolysis of the monobromo ester (II,  $R=CO_2Me$ ,  $R'=H$ ) with cold alkali. The bromo-acid could not be methylated.

7-Methoxy-4-methylcoumarin-6-carboxylic acid (I,  $R=COOH$ ,  $R'=Me$ ) which could not be obtained by the methylation of the corresponding hydroxy-acid, was obtained by the hydrolysis of the methoxy ester I ( $R=CO_2Me$ ,  $R'=Me$ ). This on bromination with

one molecule of bromine gave the 3-bromo-acid, identical with the product obtained on hydrolysis of the monobromo ester II ( $R=CO_2Me$ ,  $R'=Me$ ) with cold alkali.

The ester (I,  $R=CO_2Me$ ,  $R'=H$ ) on bromination with excess of liquid bromine gave the 3:8-dibromo compound (III,  $R=CO_2Me$ ,  $R'=H$ ) which was methylated to III ( $R=CO_2Me$ ,  $R'=Me$ ). This could not, however, be obtained by the direct bromination of the methoxy ester I ( $R=CO_2Me$ ,  $R'=Me$ ). The acid (I,  $R=CO_2H$ ,  $R'=H$ ) on bromination with excess of liquid bromine gave the 3:8-dibromo compound III ( $R=CO_2H$ ,  $R'=H$ ) which was identical with the product obtained on hydrolysis of the dibromo ester III ( $R=CO_2Me$ ,  $R'=H$ ) with cold alkali. The methoxy-dibromo ester (III,  $R=CO_2Me$ ,  $R'=Me$ ) on hydrolysis with cold alkali gave the methoxy-dibromo acid III ( $R=CO_2H$ ,  $R'=Me$ ). This could not, however, be obtained by the direct bromination of the acid (I,  $R=CO_2H$ ,  $R'=Me$ ).

The presence of the bromine atom in the 3-position has been shown by hydrolysis of the bromo-esters to the coumarilic acid derivatives. In the case of the dibromo compounds, the other bromine atom can only enter the 8-position which is *ortho* to the hydroxyl group and therefore the structure of 3:8-dibromocoumarin is assigned to the dibromo products.

No tribromo derivative could be obtained on bromination of the ester (I,  $R=CO_2Me$ ,  $R'=H$ ) and the acid (I,  $R=CO_2H$ ,  $R'=H$ ) with excess of bromine under different conditions e.g. in presence of sodium acetate, in presence of iron wire, by refluxing with bromine in acetic acid, and so on.

Attempts to decarboxylate the monobromo acid (II,  $R=CO_2H$ ,  $R'=H$ ) and the dibromo acid (III,  $R=CO_2H$ ,  $R'=H$ ) by heating in a sealed tube with water, with dilute hydrochloric acid and by heating with quinoline and copper powder did not succeed.

Attempts to prepare methyl 7-methoxy-3:8-dibromo-4-methylcoumarin-6-carboxylate (III,  $R=CO_2Me$ ,  $R'=Me$ ) and 7-methoxy-3:8-dibromo-4-methylcoumarin-6-carboxylic acid (III,  $R=CO_2H$ ,  $R'=Me$ ) by the bromination of methyl 7-methoxy-4-methylcoumarin-6-carboxylate and the corresponding acid were made under different conditions but they did not succeed, either demethylation or hydrolysis of the ester took place.

It has been found that the coumarilic acids are best obtained from the methoxybromocoumarins. The corresponding hydroxybromocoumarins generally give pasty products on hydrolysis.

#### EXPERIMENTAL

**7-Hydroxy-3-bromo-4-methylcoumarin** (II,  $R=R'=H$ ).—7-Hydroxy-4-methylcoumarin (1.76 g.), prepared according to Pechmann and Duisberg (*Ber.*, 1883, **16**, 2122), was dissolved in acetic acid (10 c.c.) by heating and bromine (1.6 g., 1 mol.) in acetic acid (16 c.c.) added gradually with shaking to the hot solution. The reaction mixture was then allowed to cool, when needles of the bromo compound separated out. It was crystallised from dilute alcohol in colorless needles, m.p. 213–15°. (Found: Br, 31.3.  $C_{10}H_7O_3Br$  requires Br, 31.4 per cent). Fries and Nohren (*loc. cit.*) give m.p. 213°. It gives a blue fluorescence with concentrated sulphuric acid and forms yellow alkali salts whose dilute solutions show a bluish green fluorescence.

The methyl ether, m.p. 147°, obtained by refluxing the compound with methyl iodide in acetone solution in presence of anhydrous potassium carbonate, was found to be identical, on direct comparison, with 7-methoxy-3-bromo-4-methylcoumarin prepared according to Limaye and Bhide (*loc. cit.*).

**7-Hydroxy-3:6-dibromo-4-methylcoumarin** (II, R—Br, R'—H) and **7-Hydroxy-3:8-dibromo-4-methylcoumarin** (III, R=R'=H).—7-Hydroxy-4-methylcoumarin (1.76 g., 1 mol.) was dissolved in acetic acid (10 c.c.) by heating and bromine (3.2 g., 2 mols.) in acetic acid (32 c.c.) added gradually with shaking to the hot solution. The reaction mixture was then heated on a boiling water-bath for two hours when a solid separated out which was filtered off on cooling, m.p. 240°-260°. This was refluxed with acetic acid (50 c.c.) for 15 minutes when a part of it dissolved. The solution was filtered while hot and the filtrate allowed to cool. This was worked up as given below. The residue was crystallised from acetic acid in colorless, shining, elongated plates, m.p. 274-76°, yield 0.5 g. This is 7-hydroxy-3:8-dibromo-4-methylcoumarin. (Found: Br, 47.7.  $C_{10}H_6O_3Br_2$  requires Br, 47.9 per cent).

The crystals which separated out from the filtrate (from above) on cooling were recrystallised from acetic acid in small white needles, m.p. 246-48°, yield 1 g. This is 7-hydroxy-3:6-dibromo-4-methylcoumarin. (Found: Br, 47.5.  $C_{10}H_6O_3Br_2$  requires Br, 47.9 per cent).

Both the compounds form yellow salts with alkalis, dilute solutions of which show a faint bluish green fluorescence.

Both the above compounds were obtained on further bromination of 7-hydroxy-3-bromo-4-methylcoumarin. They also gave 7-hydroxy-3:6:8-tribromo-4-methylcoumarin on further bromination.

**7-Methoxy-3:8-dibromo-4-methylcoumarin** (III, R—H, R'—Me) was prepared by methylation of 7-hydroxy-3:8-dibromo-4-methylcoumarin with methyl iodide as usual. It was crystallised from acetic acid, m.p. 235°. (Found: Br, 45.7.  $C_{11}H_8O_3Br_2$  requires Br, 46.0 per cent).

**7-Methoxy-3:6-dibromo-4-methylcoumarin** (II, R—Br, R'—Me), prepared by methylating 7-hydroxy-3:6-dibromo-4-methylcoumarin with methyl iodide as usual, gave m.p. 240°. Mixed melting point with the dibromo compound obtained from 7-methoxy-4-methylcoumarin according to Limaye and Bhide (*loc. cit.*) was not lowered. The constitution of this compound was proved by synthesis from 4-bromoresorcinol as follows.

4-Bromoresorcinol was prepared according to the method of Sandin and McKee ("Organic Syntheses", 1937, Vol. XVII, pp. 23-24) and condensed with ethyl acetoacetate in presence of sulphuric acid (Chakravarti and Mukerjee, *loc. cit.*) to get 7-hydroxy-6-bromo-4-methylcoumarin. This was methylated with dimethyl sulphate and alkali (Chakravarti and Mukerjee, *loc. cit.*) when 7-methoxy-6-bromo-4-methylcoumarin resulted. This was brominated with one molecule of bromine in acetic acid to get 7-methoxy-3:6-dibromo-4-methylcoumarin.

**6-Methoxy-7-bromo-3-methylcoumarilic Acid** (IV, R=H, R'=Me, R''=Br).—7-Methoxy-3:8-dibromo-4-methylcoumarin (1 g.) was refluxed with potassium hydroxide solution (1N, 20 c.c.) for 2 hours. It was then cooled and acidified with concentrated hydrochloric acid.



The precipitated solid was crystallised from acetic acid in small white prisms, m.p.  $252^{\circ}$  (decomp.), yield 0.4 g. (Found: Br, 28.3.  $C_{11}H_8O_4Br$  requires Br, 28.1 per cent). It gives a blue coloration with concentrated sulphuric acid on warming.

*6-Methoxy-5-bromo-4-methylcoumarilic acid* (IV, R = Br, R' = Me, R'' = H).—7-methoxy-3:6-dibromo-4-methylcoumarin (1 g.) was refluxed with sodium hydroxide solution (10%, 20 c.c.) for two hours. The solution was then cooled and acidified with concentrated hydrochloric acid. The solid obtained was crystallised from acetic acid in small white needles, m.p.  $256^{\circ}$  (decomp.), yield 0.5 g. Limaye and Bhide (*loc. cit.*) give the same melting point.

*7-Hydroxy-3:6:8-tribromo-4-methylcoumarin* (III, R = Br, R' = H).—7-Hydroxy-4-methylcoumarin (2 g.) was placed in a flask and liquid bromine (3 c.c., excess) added. There was a copious evolution of hydrogen bromide fumes. The mixture was then kept overnight. The residual solid was treated with a strong solution of sodium bisulphite to remove the excess of bromine. The product obtained was crystallised from acetic acid in small, colorless, shining plates, m.p.  $250-52$ , yield 2.5 g. (Found: Br, 58.4.  $C_{10}H_5O_3Br_3$  requires Br, 58.1 per cent). It forms yellow alkali salts, dilute solutions of which give a faint bluish green fluorescence.

This compound was also obtained when 7-hydroxy-4-methylcoumarin was brominated with one molecule of bromine in presence of sodium acetate and by further bromination of the 3:6 and 3:8-dibromocoumarins.

*7-Methoxy-3:6:8-tribromo-4-methylcoumarin* (III, R = Br, R' = Me).—7-Methoxy-4-methylcoumarin (2 g.) was gently refluxed on a water-bath with liquid bromine (5 c.c., excess) for 4 hours. The bromine was then allowed to evaporate and the residual solid was treated with a 5% solution of sodium hydroxide to remove the demethylated product. The insoluble product was then filtered and washed several times with water to remove the adhering sodium salt of the demethylated product and then crystallised from acetic acid in colorless, cubic plates, m.p.  $196-98^{\circ}$ , yield 0.8 g. (Found: Br, 56.5.  $C_{11}H_7O_3Br_3$  requires Br, 56.2 per cent). Mixed melting point with 7-methoxy-3:6:8-tribromo-4-methylcoumarin, obtained by methylation of 7-hydroxy-3:6:8-tribromo-4-methylcoumarin, was not depressed.

*6-Methoxy-5:7-dibromo-3-methylcoumarilic Acid* (IV, R = R'' = Br, R' = Me).—7-Methoxy-3:6:8-tribromo-4-methylcoumarin (1 g.) was refluxed with potassium hydroxide solution (1N, 20 c.c.) for two hours. The resulting solution was cooled and acidified with concentrated hydrochloric acid. The precipitated solid was crystallised from acetic acid in small, white cubes, m.p.  $268^{\circ}$  (decomp.), yield 0.5 g. (Found: Br, 43.7.  $C_{11}H_8O_4Br_2$  requires Br, 44.0 per cent). It gives a blue coloration on warming with sulphuric acid.

*7-Methoxy-4-methylcoumarin-6-carboxylic Acid* (I, R =  $CO_2H$ , R' = Me).—Methyl 7-methoxy-4-methylcoumarin-6-carboxylate (10 g.), prepared according to Shah *et al.* (*loc. cit.*), was heated on a boiling water-bath with sodium hydroxide solution (10%, 100 c.c.) for half an hour when the ester went into solution completely. The solution was cooled, filtered and acidified with concentrated hydrochloric acid. The precipitated solid was filtered and crystallised from acetic acid in small needles, m.p.  $268-70^{\circ}$  (decomp.), yield 6 g. (Found: C, 61.1; H, 4.3.  $C_{12}H_{10}O_6$  requires C, 61.5; H, 4.3 per cent).

*Methyl 7-Hydroxy-3-bromo-4-methylcoumarin-6-carboxylate* (II,  $R = CO_2Me$ ,  $R' = H$ ).—Methyl 7-hydroxy-4-methylcoumarin-6-carboxylate (2.34 g.) was dissolved in acetic acid (10 c.c.) by heating and bromine (1.6 g., 1 mol.) dissolved in acetic acid (16 c.c.) added gradually with shaking to the hot solution. The reaction mixture was kept overnight when crystals of the monobromo compound separated out. Crystals from acetic acid, m.p. 196-98°, yield 2.0 g. (Found: Br, 25.3.  $C_{12}H_9O_5Br$  requires Br, 25.6 per cent).

This compound was methylated with methyl iodide in the usual manner and the methyl ether found to be identical, on direct comparison, with methyl 7-methoxy-3-bromo-4-methylcoumarin-6-carboxylate (described below).

*Methyl 7-Methoxy-3-bromo-4-methylcoumarin-6-carboxylate* (II,  $R = CO_2Me$ ,  $R = Me$ ).—Methyl 7-methoxy-4-methylcoumarin-6-carboxylate (2.48 g.) was dissolved in acetic acid (20 c.c.) by heating and bromine (1.6 g., 1 mol.) in acetic acid (16 c.c.) added gradually with shaking to the hot solution. The crystals of the monobromo compound obtained on keeping the reaction mixture overnight were crystallised from acetic acid in silky, white needles, m.p. 208-10°, yield 2.4 g. (Found: Br, 24.8.  $C_{13}H_{11}O_5Br$  requires Br, 24.5 per cent).

*6-Methoxy-3-methyl-5-carboxylcoumarilic Acid* (IV,  $R = CO_2H$ ,  $R = Me$ ,  $R'' = H$ ).—Methyl 7-methoxy-3-bromo-4-methylcoumarin-6-carboxylate (1g.) was refluxed with potassium hydroxide solution (1N, 20 c.c.) for two hours on a wire gauze. The solution was then cooled, filtered and acidified with concentrated hydrochloric acid. The precipitated solid was crystallised from acetic acid in small, white needles, m.p. 288 (decomp.), yield 0.5 g. (Found: C, 57.4; H, 4.2.  $C_{12}H_{10}O_6$  requires C, 57.6; H, 4.0 per cent). It gives a violet coloration when warmed with concentrated sulphuric acid.

*7-Hydroxy-3-bromo-4-methylcoumarin-6-carboxylic Acid* (II,  $R = CO_2H$ ,  $R' = H$ ).—7-Hydroxy-4-methylcoumarin-6-carboxylic acid (2.2 g.) was suspended in hot acetic acid (20 c.c.) and bromine (1.6 g., 1 mol.) in acetic acid (16 c.c.) added gradually with shaking to the hot suspension, when the acid gradually went into solution. The reaction mixture was kept overnight and the solid which separated out was crystallised from dilute alcohol in small, colorless needles, m.p. 260° (decomp.), yield 1.7g. (Found: Br, 26.9.  $C_{11}H_7O_5Br$  requires Br, 26.8 per cent).

This acid was also obtained when methyl 7-hydroxy-3-bromo-4-methylcoumarin-6-carboxylate was hydrolysed by keeping with 5% alkali for 40 hours at room temperature.

*7-Methoxy-3-bromo-4-methylcoumarin-6-carboxylic Acid* (II,  $R = CO_2H$ ,  $R' = Me$ ).—7-Methoxy-4-methylcoumarin-6-carboxylic acid (2.34 g.) was dissolved in acetic acid (50 c.c.) and bromine (1.6 g., 1 mol.) in acetic acid (16 c.c.) added gradually with shaking to the hot solution. The reaction mixture was then heated on a boiling water-bath for an hour and then allowed to stand overnight. The solid which separated out was crystallised from acetic acid in white needles, m.p. 263-65° (decomp.), yield 2.4 g. (Found: Br, 25.4.  $C_{12}H_9O_5Br$  requires Br, 25.6 per cent).

This acid was also obtained by hydrolysing methyl 7-methoxy-3-bromo-4-methylcoumarin-6-carboxylate with dilute alkali at room temperature.

*Methyl 7-Hydroxy-3:8-dibromo-4-methylcoumarin-6-carboxylate* (III,  $R = CO_2Me$ ,  $R' = H$ ).—Methyl 7-hydroxy-4-methylcoumarin-6-carboxylate (2 g.) was placed in a flask and liquid bromine (5c.c., excess) added gradually to it. The reaction mixture was kept overnight at room temperature. The residual solid after treatment with sodium bisulphite solution was crystallised from acetic acid in tiny, white needles, m.p.  $240-42^\circ$ , yield 2.6 g. (Found : Br, 40.7.  $C_{12}H_8O_5Br_2$  requires Br, 40.8 per cent).

The *methyl ether* was prepared by refluxing it in acetone solution with methyl iodide in presence of anhydrous potassium carbonate for 20 hours. It was crystallised from acetic acid, m.p.  $184-86$ . (Found : Br, 39.6.  $C_{13}H_{10}O_5Br_2$  requires Br, 39.4 per cent).

*6-Methoxy-7-bromo-3-methyl-5-carboxylcoumarilic Acid* (IV,  $R = CO_2H$ ,  $R' = Me$ ,  $R'' = Br$ ).—Methyl 7-methoxy-3:8-dibromo-4-methylcoumarin-6-carboxylate (1 g.) was refluxed with potassium hydroxide solution (1N, 20 c.c.) for 2 hours. The solid obtained on acidification was crystallised from acetic acid in small, white cubes, m.p.  $278$  (decomp.). (Found : Br, 24.6.  $C_{12}H_9O_6Br$  requires Br, 24.3 per cent). It gives a violet coloration when warmed with concentrated sulphuric acid.

*7-Hydroxy-3:8-dibromo-4-methylcoumarin-6-carboxylic Acid* (III,  $R = CO_2H$ ,  $R' = H$ ).—7-Hydroxy-4-methylcoumarin-6-carboxylic acid (2.2 g.) was suspended in acetic acid (20 c.c.) and bromine (3.2g., 2mols.) in acetic acid (32c.c.) added. The reaction mixture was then gently refluxed on a wire gauze for two hours. The solid which separated on cooling was crystallised from acetic acid in small, white needles, m.p.  $286^\circ$  (decomp.), yield 2.3 g. (Found: Br, 42.7.  $C_{11}H_6O_5Br_2$  requires Br, 42.3 per cent).

*7-Methoxy-3:8-dibromo-4-methylcoumarin-6-carboxylic Acid* (III,  $R = CO_2H$ ,  $R' = Me$ ).—Methyl 7-methoxy-3:8-dibromo-4-methylcoumarin-6-carboxylate (0.5 g.) was kept with sodium hydroxide solution (5%, 20c.c.) for 40 hours when the ester went into solution. The solution was filtered and acidified with concentrated hydrochloric acid. The precipitated solid was crystallised from acetic acid in shining, white needles, m.p.  $248-50$  (decomp.). (Found : Br, 40.5.  $C_{12}H_8O_5Br_2$  requires Br, 40.8 per cent).

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## SEARCH FOR NEW INSECTICIDES. PART IV

BY A. B. SEN AND P. M. BHARGAVA

5-Chloro-(I), 3:5-dichloro-(II), 4-methyl-5-chloro-(III) and 5-*o*-*o*-*o*-tetrachloro-(IV) 2-hydroxy-acetophenones have been prepared by Fries reaction. 3-Chloro-2-hydroxyacetophenone (V) and (I) have been obtained by the Friedel-Crafts reaction between acetyl chloride and *o*- and *p*-chlorophenols respectively, and subsequent hydrolysis of the acetates formed. Methyl, ethyl and propyl ethers of (I), (II), (III) and (V) have been prepared.

In extension of our previous work on this subject (this *Juornal*, 1948, **25**, 277 ; 1949, **26**, 243, 287) we have now synthesised a number of halogen-substituted hydroxyacetophenones and their alkyl ethers with a view to studying them for their possible insecticidal action. These compounds are expected to possess good insecticidal action as they contain in their molecule the residues of different inhalation narcotics (viz.,  $\text{CCl}_3$ ,  $\text{COCH}_3$ ,  $\text{COCCl}_3$ ,  $\text{OCH}_3$  etc.) attached to the poisonous chlorobenzene ring ; that this type of combination is essential for a good contact insecticide is already known (Busvine, *Nature*, 1935, **156**, 169). Five hydroxyketones, viz., 5-chloro-(I), 3:5-dichloro-(II), 4-methyl-5-chloro-(III), 5-*o*-*o*-*o*-tetrachloro-(IV) and 3-chloro-(V) 2-hydroxy-acetophenones have been prepared ; (I), (II), (III) and (V) have been subsequently converted into their methyl, ethyl and propyl ethers. It may be mentioned that a number of alkyl halogen phenols have already been shown to possess good bactericidal properties (Klarman, Shternov and Gates, *J. Amer. Chem. Soc.*, 1933, **55**, 2576).

(I), (II), (III) and (V) have been prepared by the Fries rearrangement of the corresponding acetates. The first three of these compounds have been previously obtained by this method by several authors (Wittig, *Ber.*, 1924, **57**, 88, 1270 ; *Annalen*, 1926, **446**, 155; Karrer *et al.*, *Helv. Chim. Acta*, 1930, **13**, 1308 ; Klarman *et al.*, *loc. cit.* Chien and Yin, *J. Chinese Chem. Soc.*, 1939, **7**, 40 ; Rosenmund and Schnurr, *Annalen*, 1928, **460**, 56). *o*-Chlorophenyl acetate could not be rearranged even on heating at  $140^\circ$  for 8 hours with  $1\frac{1}{2}$  mole of anhydrous aluminium chloride.

The Friedel-Crafts reaction between acetyl chloride and *p*- and *o*- chlorophenols in presence of anhydrous aluminium chloride resulted in a formation of the acetates of 5-chloro- and 3-chloro-2-hydroxy-acetophenones respectively in very good yields (cf. Nencki and Stoeber, *Ber.*, 1897, **30**, 1771 ; Claus, *Chem. Zentr.* 1898, **11**, 158; these authors have carried out the above reaction in presence of anhydrous ferric chloride, and obtained 5-chloro-2-hydroxy- and 3-chloro-4-hydroxy- acetophenones in the case of *p*- and *o*- chlorophenols respectively). These acetates yielded the corresponding phenols on hydrolysis with alkali.

The methyl, ethyl and propyl ethers of (I), (II), (III) and (V) were obtained in good yields (60-90%) by using dimethyl sulphate, ethyl iodide and propyl bromide respectively. Methyl ethers of 2-hydroxy-5-chloro- and 2-hydroxy-4-methyl-5-chloro- acetophenones have been previously described, the former having been obtained by the action of acetyl chloride on

methyl ether of *p*-chlorophenol in presence of anhydrous aluminium chloride (Wittig, *Ber.*, 1924, **57**, 93) or by methylation of the corresponding hydroxy compound with methyl iodide (Chakravarti and Dutta, *J. Indian Chem. Soc.*, 1940, **17**, 66), and the latter by the methylation of 2-hydroxy-5-chloro-4-methylacetophenone by dimethyl sulphate (Wittig, *Annalen*, 1926, **446**, 155).

All the *o*-hydroxyacetophenones prepared, gave the Pyman's test (Gulthard, Marshall and Pyman, *J. Chem. Soc.*, 1930, 280) for *o*-hydroxy- ketones and also gave intense violet coloration with 1% ferric chloride. The ethers obtained are insoluble in water, dilute alkali or acids, but dissolve in all common organic solvents.

#### EXPERIMENTAL

*Acetates of the Halogen-substituted Phenols.*—*p*-Chlorophenyl acetate (b.p. 127°/22mm.) was obtained from *p*-chlorophenol (32.1 g.), acetic anhydride (24 c.c.) and anhydrous sodium acetate (10 g.) by the method of Wohlleben (*Ber.*, 1910, **43**, 4372, b.p. 108°/12.5 mm.) in nearly theoretical yield. The acetate of 3-methyl-4-chlorophenol (b.p. 143°-145°/17-18 mm.) was similarly prepared from the phenol (20g.), acetic anhydride (22 c.c.) and sodium acetate (8 g.) in approximately theoretical yield (Nathan Sulzberger, A.P. 149860; *Chem. Zentr.*, 1927, II, 1893, who used concentrated sulphuric acid as the dehydrating agent, reports b.p. 241°-243°). 2:4-Dichlorophenyl acetate (b.p. 135°-137°/18-19 mm.) was obtained by the method of Fischer (*Ann. Spl.* 7, 184, b.p. 244°-245°; Chien and Yin, *loc. cit.*, give b.p. 167°-168°/80mm.) from 32.6 g. of the phenol and 30 g. of acetyl chloride by heating to 50-60° for about 2 hours, the yield being 78.3% of theory. In all the above cases, the acetate was isolated by extraction with ether and distillation in vacuum, after removal of the ether from the dried ethereal extract.

The trichloroacetate of *p*-chlorophenol (b.p. 115°/20mm.) was prepared by the method described by us previously (this *Journal*, 1948, **25**, 280).

*Fries Rearrangement of the Acetates of the Halogen-substituted Phenols.*—The acetate (1*M*) and anhydrous aluminium chloride (2*M* approx.) were taken in a 500 c.c. pyrex flask fitted with a reflux condenser, and the contents of the flask gradually heated, first over a water-bath and then in an oil-bath, the temperature being raised to 125° during the course of an hour and maintained between 125° and 130° for about 3 hours (excepting in the case of 3-methyl-4-chlorophenylacetate, which required only 1 hour at this temperature to rearrange). The contents of the flask were then cooled, treated with ice and hydrochloric acid and left overnight for the decomposition to be complete. The oil separating (a semi-solid mass in some cases) was extracted with ether and the ethereal extract washed, dried and filtered. On removal of the ether from the filtrate and distillation of the residual liquid in vacuum, the *ortho*-hydroxyacetophenone corresponding to the acetate used, was obtained. The ketones thus prepared are described in Table I.

*Acetates of 5-Chloro- and 3-Chloro-2-hydroxyacetophenones.*—These compounds were obtained by the action of acetyl chloride on *p*- and *o*-chlorophenols respectively, in presence of anhydrous aluminium chloride as described below.

The *p*- or *o*-chlorophenol was covered with petrol-ether (50-75 c.c.) in a 250 c.c. flask, cooled in ice, and aluminium chloride ( $1\frac{1}{2}$ -2 moles) added. The flask was then attached to a reflux condenser and acetyl chloride (1-2 moles) added dropwise from the top of the condenser. After the brisk reaction had subsided (which takes about one hour), the contents of the flask were refluxed over a water-bath for 2 hours and left overnight. On distilling off the petrol ether from the mixture and decomposing the residue with dilute hydrochloric acid as usual, a dark coloured oil was obtained, which was extracted with ether. The ethereal extract was well washed with water, dried over calcium chloride, filtered and the ether removed. The acetate of the chloro-*o*-hydroxyacetophenone corresponding to the chlorophenol used, was obtained on distilling the residual liquid in vacuum.

The acetate of 5-chloro-2-hydroxyacetophenone was thus obtained as a colorless liquid, b.p.  $144^{\circ}$ - $146^{\circ}$ /1mm., from *p*-chlorophenol (13 g.), acetyl chloride (14g.) and aluminium chloride (23 g.) (Wittig, *Annalen*, 1926, **446**, 155, who obtained this compound from 2-acetyl-4-chlorophenol, acetyl chloride and calcium chloride, gave b.p.  $156^{\circ}$ - $157^{\circ}$ /14mm.), yield 17g. (79% of theory). (Found: C, 56.13; H, 4.11; Cl, 16.67. Calc. for  $C_{10}H_7O_3Cl$ : C, 56.57; H, 4.23; Cl, 16.75 per cent).

The acetate of 3-chloro-2-hydroxyacetophenone was similarly obtained from *o*-chlorophenol (26 g.), acetyl chloride (28 g.) and aluminium chloride (46 g.), as a colorless liquid, b.p.  $151^{\circ}$ - $154^{\circ}$ /1mm., yield 35.6 g. (82.8% of theory). (Found: C, 56.14; H, 4.09; Cl, 16.27.  $C_{10}H_7O_3Cl$  requires C, 56.47; H, 4.23; Cl, 16.75 per cent).

5-Chloro- and 3-Chloro-2-hydroxyacetophenones (by hydrolysis of the acetates).—The acetates, described above, yielded the free phenols on hydrolysing with 20% caustic potash solution (4 c.c. for every g. of the acetate) for half an hour. The resulting solution was cooled and acidified with hydrochloric acid, and the oil that separated out, was extracted with ether. The ethereal extract was washed, dried over calcium chloride, filtered and the ether removed from the filtrate. The chlorohydroxyacetophenone was obtained on distilling the residual liquid in vacuum.

The acetate of 5-chloro-2-hydroxyacetophenone, thus on hydrolysis, yielded 5-chloro-2-hydroxyacetophenone, b.p.  $126$ - $128^{\circ}$ /28mm. (described elsewhere also in this paper), yield 90.7% of theory. (Found: C, 56.02; H, 3.87; Cl, 20.91. Calc. for  $C_8H_7O_2Cl$ : C, 56.30; H, 4.11, Cl, 20.82 per cent).

3-Chloro-2 hydroxyacetophenone (b.p.  $87$ - $89^{\circ}$ /1 mm.) was similarly obtained from the corresponding acetate as a colorless liquid, yield 93.5% of theory. (Found: C, 56.17; H, 4.07; Cl, 20.93.  $C_8H_7O_2Cl$  requires C, 56.30; H, 4.11; Cl, 20.82 per cent).

Alkyl Ethers of Substituted Hydroxyacetophenones.—The methyl ethers were prepared from the hydroxy compound (4.5 g.), 10% caustic soda solution (containing approximately  $1\frac{1}{2}$  to 2 times the requisite amount of alkali) and dimethyl sulphate ( $1\frac{1}{2}$  to 2 times the requisite amount) by the usual method. The reagents were heated for 5 hours under continuous stirring and then left overnight. The oil separating after dilution with water was extracted with ether. The ethereal extract was washed and dried and the ether removed as usual. The methyl ether was obtained on distilling the residual liquid in vacuum.

TABLE I

Ketone.	I	II	III	IV	Obtained from acc.-AlCl <sub>3</sub>	B.p.	Yield (% of theory).	Properties of the liquid.	Formula	Found (%)			Calc. (%)		
										C.	H.	Cl.	C.	H.	Cl.
I	35 g.	54.5 g.	107-109°, 12 mm.	51.4	Colorless, solidifying on chilling in ice.	C <sub>10</sub> H <sub>7</sub> O <sub>2</sub> Cl	56.10	3.93	20.61	56.30	4.11	20.82	56.30	4.11	20.82
II	27	34.5	132°-134°, 18	70.4	Colorless, solidifying to white crystals on cool- ing in ice.	C <sub>10</sub> H <sub>7</sub> O <sub>2</sub> Cl	46.63	2.67	34.41	46.83	2.92	34.63	46.83	2.92	34.63
III	22	32	140°-142°, 21	63.6	Colorless, solidifying to white crystals on cooling in ice.	C <sub>10</sub> H <sub>7</sub> O <sub>2</sub> Cl	58.14	4.63	19.43	58.53	4.88	19.24	58.53	4.88	19.24
IV	18	18	129-32°, 44	25	Brilliant yellow liquid, turning brown in a few weeks	C <sub>10</sub> H <sub>7</sub> O <sub>2</sub> Cl	34.81	1.59	51.61	35.04	1.46	51.82	35.04	1.46	51.82

I = 5-chloro-2-hydroxyacetophenone (Klarmann. Sherron and Gates, *loc. cit.*, give b.p. 97-99°/2 mm.).  
 II = 3,5-dichloro-2-hydroxyacetophenone (Chien and Yin, *loc. cit.*, give m. p. 95-96°).  
 III = 4-methyl-5-chloro-2-hydroxyacetophenone (Rosenmund and Schnorr, *loc. cit.*, give b. p. 137/15 mm.).  
 IV = 5-*o*-tetrachloro-2-hydroxyacetophenone.

TABLE II

Name.	B.p.	Yield (%) of theory).	Properties of the liquid.	Formula.	C.	Found (%)		Cl. <sup>-</sup>	C.	Calculated (%)	
						H.	Cl.			H.	Cl.
Methyl ether of I*	108°/2 mm.	79.2	Colorless, solidifying on cooling in ice.	C <sub>10</sub> H <sub>11</sub> O <sub>2</sub> Cl	58.17	4.76	19.01	58.53	4.88	19.24	
Ethyl ether of I	142°/1 <sub>1</sub>	63.2	Colorless	C <sub>10</sub> H <sub>11</sub> O <sub>2</sub> Cl	60.24	5.51	18.46	60.45	5.54	17.88	
Propyl ether of I	110-12°/1	84.4	"	C <sub>10</sub> H <sub>11</sub> O <sub>2</sub> Cl	61.93	6.07	16.36	62.12	6.11	16.70	
Methyl ether of II	148°/43	91.4	"	C <sub>10</sub> H <sub>11</sub> O <sub>2</sub> Cl	48.89	3.52	32.40	49.31	3.61	32.42	
Ethyl ether of II	175°/2	64.7	"	C <sub>10</sub> H <sub>11</sub> O <sub>2</sub> Cl <sub>2</sub>	51.81	4.19	30.26	51.50	4.29	30.47	
Propyl ether of II	142°/2	51.5	"	C <sub>10</sub> H <sub>11</sub> O <sub>2</sub> Cl <sub>2</sub>	53.41	4.67	29.40	53.44	4.85	29.15	
Methyl ether of III†	111°/0.5	75.4	Colorless, solidifying on cooling in ice.	C <sub>10</sub> H <sub>11</sub> O <sub>2</sub> Cl	60.19	5.39	17.79	60.45	5.54	17.88	
Ethyl ether of III	160°/4	70.0	Pale yellow	C <sub>10</sub> H <sub>11</sub> O <sub>2</sub> Cl	61.91	6.01	16.56	62.12	6.11	16.70	
Propyl ether of III	158°/2	55.0	Pale yellow	C <sub>10</sub> H <sub>11</sub> O <sub>2</sub> Cl	63.39	6.41	15.43	63.62	6.62	15.67	
Methyl ether of V	88°/1	68.6	Colorless	C <sub>10</sub> H <sub>11</sub> O <sub>2</sub> Cl	58.09	4.67	19.42	58.53	4.88	19.24	
Ethyl ether of V	91-93°/1	72.1	Colorless, turning red and then brown on keeping.	C <sub>10</sub> H <sub>11</sub> O <sub>2</sub> Cl	60.24	5.37	18.06	60.45	5.54	17.88	
Propyl ether of V	108-10°/1	47.0	Colorless.	C <sub>10</sub> H <sub>11</sub> O <sub>2</sub> Cl	62.07	5.91	16.33	62.12	6.11	16.70	

I-III, as referred to in Table I.

V = 3-chloro-2-hydroxyacetophenone.

\*. Wittig, *Ber.*, 1924, 57, 93, gives m.p. 29-30°; Chakravarty and Datta, *loc. cit.*, give b.p. 135°/6 mm.

†. Wittig, *Annalen*, 1926, 446, 155, gives m.p. 79-80°.

The *ethyl and propyl ethers* were prepared from 5-4 g. of the phenol, sodium ethoxide and alkyl halide ( $1\frac{1}{2}$  to 2 times the calculated amount of each of these) (ethyl iodide and propyl bromide were used for the ethyl and propyl ethers respectively) in the usual way. The reagents were refluxed for 3 hours. After removal of the excess of alcohol by distillation, the residue was cooled and extracted with ether. The ethereal extract was washed, dried, ether removed and the residual liquid distilled in vacuum when the ether corresponding to the phenol and the alkyl halide used was obtained.

The ethers that have thus been prepared are described in Table II.

The insecticidal action of the compounds, described in this paper, is under investigation.

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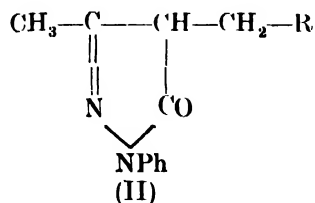
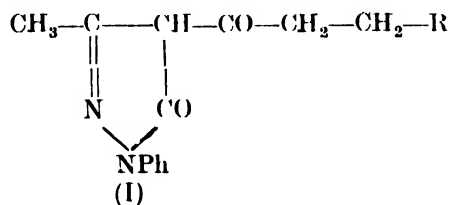
## SEARCH FOR NEW ANTISPASMODICS. PART I

BY B. PATHAK AND T. N. GHOSH

In search for new antispasmodics, some pyrazolone derivatives containing tertiary bases have been synthesised.

During recent years a number of synthetic compounds have been discovered, which exhibit antispasmodic activity. Many of these products are much simpler in structure than the naturally occurring antispasmodics, papaverine and atropine. Diethylaminoethyl esters of diphenylacetic acid and analogous compounds have been found to possess powerful antispasmodic activity (cf. Blicke, *Ann. Rev. Biochem.*, 1944, **13**, 549). Relatively simple piperidine derivatives are also known to have antispasmodic activity (Cerkovnikov and Prelog, *Ber.*, 1941, **74** 1648; Fellows and Cunningham, *Federation Proc.*, 1942, **1**, 151; Lee and Freudenberg, *J. Org. Chem.*, 1944, **9**, 537; Foster, Moench and Clark, *J. Pharm. Exp. Therap.*, 1946, **87**, 73; Kwartler and Lucas, *J. Amer. Chem. Soc.*, 1947, **69**, 2582). Thus, it appears that all the efficient antispasmodics, although differing widely in molecular structure, are, in general, salts of tertiary bases. In view of the interesting observation of Notkin and Webster (*Rev. Canadian Biol.*, 1942, **1**, 660) that amidopyrine, which is a pyrazolone derivative, possesses antispasmodic activity, it has been considered desirable to introduce tertiary bases into a pyrazolone molecule and to have the resulting products examined for any spasmolytic activity.

Ketones containing an active methyl or methylene group have been shown by Mannich (*Ber.*, 1920, **53**, 1368; 1922, **55**, 356; *Arch. Pharm.*, 1926, **264**, 741; 1927, **265**, 589) to condense with formaldehyde and secondary bases. 1-Phenyl-3-methyl-4-acetylpyrazolone (Stolz, *J. prakt. Chem.*, 1897, *ii*, **55**, 154) has now been condensed with formaldehyde and secondary bases to yield compounds of the type (I). Compounds other than ketones, but containing an active methyl or methylene group, may sometimes be induced to respond to Mannich reaction (cf. Kermack and Muir, *J. Chem. Soc.*, 1931, 3089). As 1-phenyl-3-methylpyrazolone contains a reactive methylene group (cf. Narang *et al.*, *J. Indian Chem. Soc.*, 1934, **11**, 427), this compound has been substituted for the ketone in the Mannich reaction to furnish, when allowed to react with formaldehyde and secondary bases, compounds of the type (II).



[where R is piperidino, dimethylamino or diethylamino group]. The maximum yields of the above types of compounds (I and II) attained were of the order of 55-60%, rendered possible by using 1 mol. of 1-phenyl-3-methylpyrazolone or of its 4-acetyl derivative, 1.5 mols. of formaldehyde and 1.5 mols. of the secondary base (cf. Kermack and Muir, *loc. cit.*), the

formaldehyde being in the form of commercial 40% formalin. These compounds (I and II) are amphoteric, being readily soluble in cold dilute alkali (cf. Ghosh and Das Gupta, *J. Indian Chem. Soc.*, 1939, **16**, 63) and yielding *hydrochlorides* (which are practically insoluble in water) and *methiodides*. The acidic property is evidently due to the presence of the mobile hydrogen atom in the 4-position.

#### EXPERIMENTAL

The methods of preparation of the compounds (I and II) are essentially the same in all cases. The general method of procedure followed is therefore given below in case of one particular preparation.

*1-Phenyl-3-methyl-4-(β-piperidinopropionyl)-pyrazolone* (I, R—piperidino).—A mixture of 1-phenyl-3-methyl-4-acetylpyrazolone (21.6 g.), formaldehyde (11.3 c.c., 40%), piperidine (12.8 g.) and hydrochloric acid (18 c.c., 20% w/v) in alcohol (120 c.c.) was heated on the water-bath for about 6 hours. Next day the solution was diluted with water, when a pasty solid was precipitated. It was dissolved in cold dilute alkali and extracted with benzene and then with ether to remove the pasty matter as far as possible. The alkaline solution was stirred with charcoal for about 1 hour, filtered and just acidified with acetic acid, when a solid was precipitated. It was crystallised from ethyl alcohol-ethyl acetate (1:1) in colorless, rectangular plates (yield 58%), melting at 220-21° to an orange-yellow viscous liquid. (Found: N, 13.27.  $C_{18}H_{23}O_2N_3$  requires N, 13.41 per cent). It is readily soluble in cold dilute alkali and gives a red coloration with alcoholic neutral ferric chloride.

The *hydrochloride*, which was obtained by adding the requisite quantity of hydrochloric acid to an alcoholic solution of the base, was crystallised from dilute alcohol in colorless, rectangular plates, m.p. 250-52°. (Found: Cl, 9.58.  $C_{18}H_{24}O_2N_3Cl$  requires Cl, 10.17 per cent). The *methiodide*, which was prepared in nitrobenzene solution, was crystallised from absolute alcohol in colorless needles, melting at 266-67° to a dark red liquid. (Found: I, 27.18.  $C_{18}H_{26}O_2N_3I$  requires I, 27.91 per cent). The *phenylhydrazone* was crystallised from alcohol (in which it is sparingly soluble) in colorless, rectangular plates, m.p. above 300°. (Found: N, 16.98.  $C_{21}H_{29}ON_5$  requires N, 17.37 per cent). It is readily soluble in cold dilute alkali

*1-Phenyl-3-methyl-4-(β-diethylaminopropionyl)-pyrazolone* (I, R=diethylamino) was crystallised from ethyl alcohol-ethyl acetate in colorless, rectangular plates, m.p. 212-13°, yield 60%. (Found: N, 13.61.  $C_{17}H_{23}O_2N_3$  requires N, 13.95 per cent). The *hydrochloride* melts at 254-55°. The *methiodide* melts at 268-69°. (Found: I, 27.98.  $C_{18}H_{26}O_2N_3I$  requires I, 28.66 per cent). The *phenylhydrazone* does not melt even at 300°. (Found: N, 17.52.  $C_{23}H_{29}ON_5$  requires N, 17.90 per cent).

*1-Phenyl-3-methyl-4-(β-dimethylaminopropionyl)-pyrazolone* (I, R=dimethylamino) was crystallised from ethyl alcohol-ethyl acetate in colorless, rectangular plates, m.p. 220°, yield 58%. (Found: N, 15.02.  $C_{15}H_{19}O_2N_3$  requires N, 15.38 per cent). *Hydrochloride*, m.p. 252°. *Methiodide*, m.p. 275-76° (Found: I, 29.94.  $C_{16}H_{22}O_2N_3I$  requires I, 30.60 per cent).

*1-Phenyl-3-methyl-4-piperidinomethyl-pyrazolone* (II, R—piperidino) was crystallised from alcohol in colorless, rectangular plates, m.p. 224-25°, yield 55%. (Found: N, 15.82.  $C_{16}H_{21}ON_3$  requires N, 15.5 per cent). *Hydrochloride*, m.p. 251-52° (Found: Cl, 11.02.

$C_{16}H_{22}ON_3Cl$  requires Cl, 11.56 per cent). *Methiodide*, m.p.  $279-80^\circ$  (Found : I, 30.36.  $C_{17}H_{24}O_3NI$  requires I, 30.75 per cent).

1-*Phenyl-3-methyl-4-diethylaminomethyl-pyrazolone* (II, R=diethylamino) was crystallised from alcohol in colorless, rectangular plates m.p.  $221-22^\circ$ . (Found : N, 15.87.  $C_{15}H_{21}ON_3$  requires N, 16.21 per cent). *Hydrochloride*, m.p.  $255-56^\circ$ . *Methiodide*, m.p.  $270-271^\circ$  (Found : I, 30.98.  $C_{16}H_{24}ON_3I$  requires I, 31.67 per cent).

1-*Phenyl-3-methyl-4-dimethylaminomethyl-pyrazolone* (II, R=dimethylamino) was crystallised from alcohol in colorless, rectangular plates, m.p.  $221-22^\circ$ , yield 57%. (Found : N 18.34.  $C_{13}H_{17}ON_3$  requires N, 18.18 per cent). *Hydrochloride*, m.p.  $253-254^\circ$ .

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## SYNTHESIS OF CYANINE DYES BY THE CONDENSATION OF *p*-DIETHYLAMINOBENZALDEHYDE WITH APPROPRIATE HETEROCYCLIC COMPOUNDS. PART III

BY M. Q. DOJA AND JOGESH CHANDRA BANERJEE

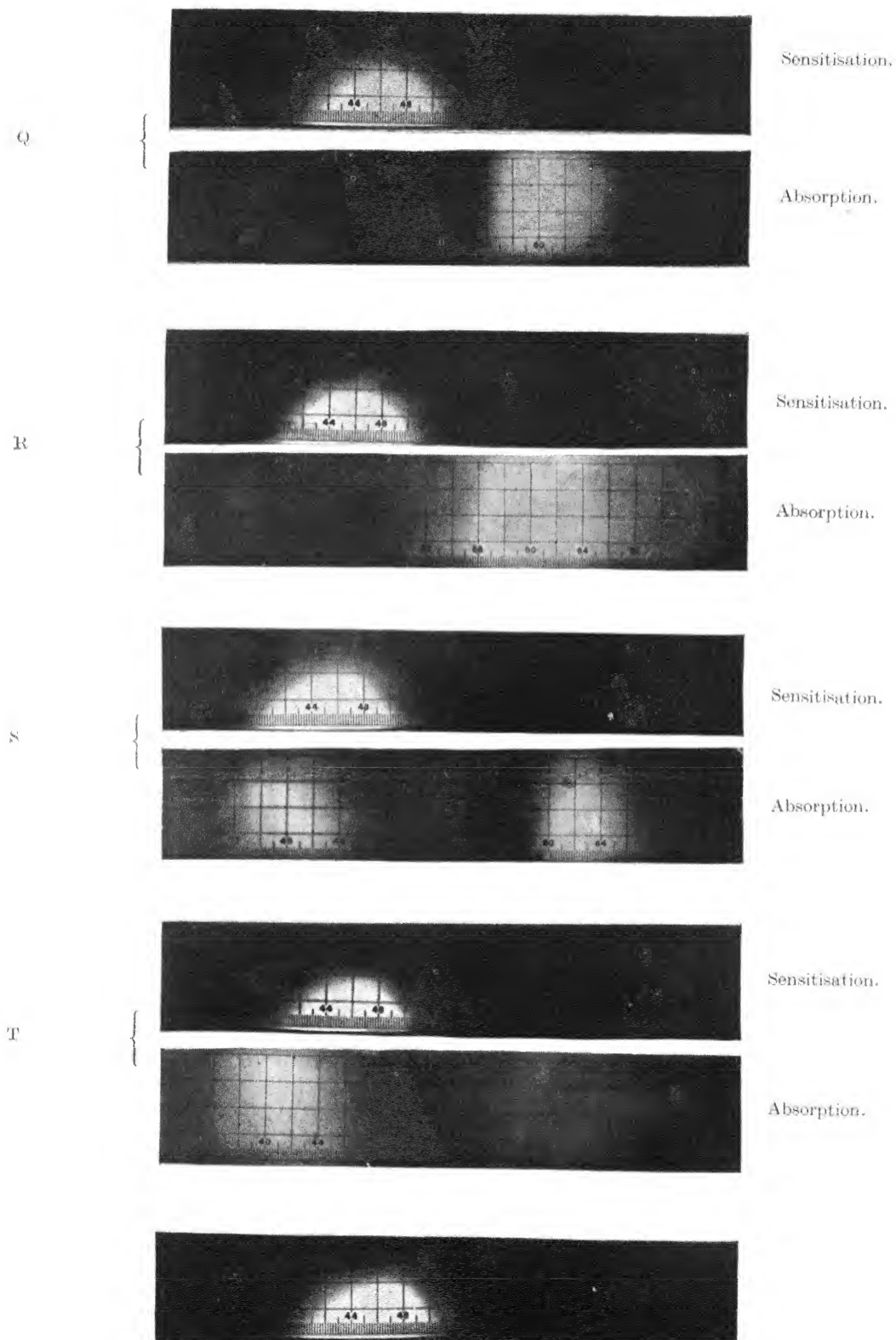
The effect on sensitisation of substitution and multiplication of groups in the thiazole and benzothiazole nuclei of *p*-diethylaminostyrylthiazole and *p*-diethylaminostyrylbenzothiazole methiodides has been studied. For this purpose four new dyes have been synthesised by condensing the methiodides of 2:5-dimethylthiazole, 2:4:5-trimethylthiazole, 2:6-dimethylbenzothiazole and 2:4:6-trimethylbenzothiazole with *p*-diethylaminobenzaldehyde. The optical, chemical, dyeing and photographic properties of these compounds have been studied. A few "intermediates" have been described.

It has been observed that the extrasensitisation, conferred on gelatino-silver bromide photographic plates by a cyanine dye, is considerably influenced by the effect of different substituent groups in different positions of the dye molecule. Thus, Mills and Pope (*Phot. J.*, 1920, **44**, 183) have observed that the introduction of a methyl group in 6-position in both 1:1'-dimethyl and 1:1'-diethylisocyanine iodides, broadens the extrasensitisation bands and heightens their intensity, while the introduction of the methyl group in the 2'-position has the opposite effect.

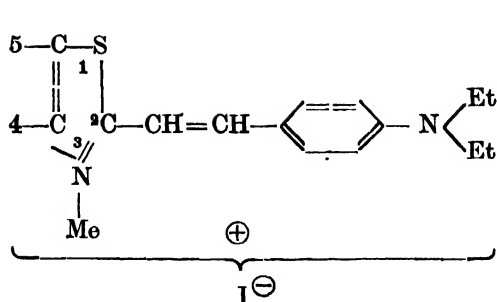
The absorption is also profoundly affected by substituents in different positions of a dye molecule. Thus, groups in 6- and 6'-positions of ethyl red are more potent in their effect than methyl and cause a greater shift, and the dimethylamino groups are the most powerful of all (cf. Meeß, "The Theory of Photographic Process", MacMillan Company, New York, 1944, p. 1022). The amino group by itself markedly augments the sensitising power of the 1:1'-dimethylisocyanine, when introduced into the 5, 6 or 6'-position though the spectrographs indicate surprisingly little difference between the effects produced by the amino-substitution in the three alternate positions. The introduction of the acetamino group in the above dye, however, has a depressing effect on the sensitising power, an effect which is influenced by the position of the substituent (Mills and Pope, *loc. cit.*).

So far no systematic investigation has been carried out on the effect of different substituent groups in the quaternised nuclei of *p*-dialkylaminostyryl type of cyanine dyes, though it is known that an increase in the molecular weight of the dye has often led to enhanced sensitisation, instances of the opposite effect being not uncommon. It was thus of interest to study the effect of substitution of different groups on sensitisation, in the quaternised thiazole and benzothiazole nuclei of 2-*p*-diethylaminostyrylthiazole methiodide (I) and 2-*p*-diethylaminostyrylbenzothiazole methiodide (II).

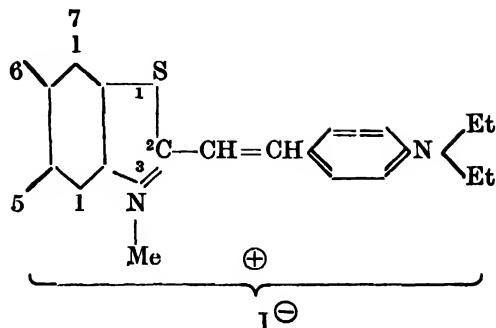
Fig 1







(I)



(II)

It will be seen that two positions, 4 and 5, are available for substitution in (I), while four positions, 4,5,6 and 7, are available in (II). Four dyes have been prepared by condensing the methiodides of 2:5-dimethylthiazole, 2:4:5-trimethylthiazole, 2:6-dimethylbenzothiazole and 2:4:6-trimethylbenzothiazole with *p*-diethylaminobenzaldehyde in absolute alcohol solution using small quantities of piperidine as catalyst. The dye (I) with a 4-methyl substitution has been described in a previous communication (Doja and Banerjee, this *Journal*, 1946, **23**, 217).

The first two methiodides containing simple thiazole systems condense less readily than the methiodides containing condensed thiazole systems (cf. Doja and Banerjee, *loc. cit.*) as the dyes in the latter case crystallise out of the alcoholic solution quite easily and are obtained in good yield after about only 6 hours of refluxing, while the dyes in the former case could not be crystallised out of the alcoholic solution even after refluxing for 72 hours and had to be precipitated out of the alcoholic solution with ether.

Some of the properties of these dyes are summarised in Table I.

The dyes are feebly soluble in cold, but more so in boiling water, and are freely soluble in alcohols and acetic acid but are insoluble in ether.

Dilute alcoholic solutions of the substituted simple thiazole dyes (Q) and (R) are orange-yellow, while those of the substituted condensed thiazoles (S) and (T) are magenta coloured. The relative intensities of dilute solutions (1:10,000) in rectified spirit, as determined by Dubosq colorimeter, are given in Table I. It will be noticed that the colour of (S) is more intense than that of (T), though the latter has an additional methyl group attached to the 4-position.

The colour of the dye solutions is reversibly discharged by the addition of mineral acids, probably due to the destruction of the conjugated systems (cf. Brooker, Sprague, Smyth and Lewis, *J. Amer. Chem. Soc.*, 1940, **62**, 1116) as indicated in a previous communication (Doja and Banerjee, *loc. cit.*). The relative resistances to decolorisation by *N*/100-HCl are given in Table I. The weaker resistance of (T) than that of (S) is perhaps due to the same effect as renders the colour of the former weaker than that of the latter.

The colour produced on cotton, wool and silk by the dyes (Q) and (R) is orange-yellow, while the dyes (S) and (T) colour them mauve. The shades, however, are not fast to washing and are discharged slowly when exposed to sunlight.

TABLE I

Com- pound.	Colour, shape & form.	Colour in cold conc. H <sub>2</sub> SO <sub>4</sub> .	M.p.	Reflex.	Pleo-chroism — Colour of light in one position of polariser.	Relative resistance to decolorisa- tion. 1 to the polariser.	Relative intensity of colour in soln.	Extra-sensitisation — Range in Å	Range in Å	Remarks.
Q	Mauve, very thin, small needles	Very faint pink	227°	Skyblue (weak)	Weak rose	Deep red	1.53	1	5100- 5900	
R	Deep magenta, stout needles	Faint yellow- ish brown	217- 18-	Greenish blue (strong)	Orange	Nearly opaque	1	1.08	5000- 5300	Indistinct Well formed crystals
S	Golden green, microscopic needles	Brownish yellow	220°	Bottle green (very strong)	Light green	Dirty green	6.74	1	Nil	Extremely beautiful crystals
T	Dark red needle clusters	Brownish yellow	215°	Yellow	Dark red	Orange-red	6.3	0.98	Nil	Some faces look like glass under polari- sed light

Q—2-*p*-Diethylaminostyryl-5-methylthiazole methiodide.  
 R—2-*p*-Diethylaminostyryl-4:5-dimethylthiazole methiodide.  
 S—2-*p*-Diethylaminostyryl-6-methylbenzothiazole methiodide.  
 T—2-*p*-Diethylaminostyryl-4:6-dimethylbenzothiazole methiodide.

TABLE II

Wallace colour filters										
	1	2	3	4	5	6	7	8	9	10
Q	Light	Deep brown red	Brownish yellow	Orange yellow	Yellowish brown	Lemon- yellow	Light green- ish brown	Light absorbed	Light absorbed	Yellowish brown
R	Do	Light absorbed	Weak yellow	Orange yellow	Lemon- yellow	Deep yellow	Greenish brown	Do	Do	Yellowish brown
S	Do	Do	Brown yellow	Brown	Weak yellow	Weak yellow	Light absorbed	Do	Do	Orange yellow
T	Do	Do	Do	Brown deep	Yellowish brown	Light yellow	Do	Do	Do	Yellow



These dyes also show the peculiar phenomenon that their acetic acid solutions deepen in colour on warming and their original colours are regained on cooling, the effect being more pronounced in aqueous acetic acid solutions (cf. Doja and Banerjee, *loc. cit.*).

Photographs of the absorption and sensitisation spectra of the dyes, as determined by a Wedge spectrograph, are shown in Fig. 1. None of the dyes is a good sensitiser. The introduction of a methyl group in the 5-position of 2-*p*-diethylaminostyrylthiazole methiodide depresses the sensitisation as compared to the 4-methyl-substituted dye. (cf. Doja and Banerjee, *loc. cit.*). The 4:5-dimethyl-substituted dye shows a still poorer sensitisation.

The 6-methyl and 4:6-dimethyl-substituted 2-*p*-diethylaminostyrylbenzothiazole methiodides show a complete depression in sensitisation as compared to the unsubstituted dye (cf. Doja and Banerjee, *loc. cit.*), which is remarkably a good sensitiser sensitising up to 6350 Å.

The fluorescence of these dyes is given in Table II. The colours noted are those of the fluorescent beam at right angles to the incident beam.

#### EXPERIMENTAL

**2:5-Dimethylthiazole methiodide.**—2:5-Dimethylthiazole, prepared from  $\alpha$ -chloropropionaldehyde and thioacetamide (*Annalen*, 1890, **259**, 240), was heated with methyl iodide (1:1.5) in a sealed tube for 24 hours. The salt crystallised from absolute alcohol in colorless, flat needles, m.p. 148°, yield 76%. (Found: I, 49.73.  $C_6H_{10}NIS$  requires I, 49.8 per cent).

**2-*p*-Diethylaminostyryl-5-methylthiazole methiodide.**—2:5-Dimethylthiazole methiodide (0.382 g.), *p*-diethylaminobenzaldehyde (0.265 g.), absolute alcohol (5 c.c.) and piperidine (2 drops) were refluxed for 8 hours. The dye was precipitated out of the solution by adding ether and was recrystallised from methyl alcohol in needles with a weak skyblue reflex, yield 32%. (Found: N, 6.70; I, 30.52.  $C_{17}H_{23}N_2IS$  requires N, 6.76; I, 30.67 per cent).

**2:4:5-Trimethylthiazole methiodide.**—2:4:5-Trimethylthiazole, prepared from methylchloroethyl ketone and thioacetamide (*Annalen*, 1888, **250**, 258) was heated with methyl iodide (1:1.5) in a sealed tube for 24 hours. The salt was recrystallised from rectified spirit in long needles, m.p. 165-66°, yield 86%. (Found: I, 47.36.  $C_7H_{12}NIS$  requires I, 47.21 per cent).

**2-*p*-Diethylaminostyryl-4:5-dimethylthiazole methiodide.**—2:4:5-Trimethylthiazole methiodide (0.95 g.), *p*-diethylaminobenzaldehyde (0.63 g.), absolute alcohol (5 c.c.) and piperidine (2 drops) were refluxed for 8 hours. The dye was precipitated out of the solution with ether and was recrystallised from methyl alcohol in needles with strong greenish blue reflex, yield 42%. (Found: N, 6.48; I, 29.51.  $C_{18}H_{25}N_2IS$  requires N, 6.54; I, 29.67 per cent).

**2:6-Dimethylbenzothiazole methiodide.**—2:6-Dimethylbenzothiazole, prepared from thioaceto-*p*-toluidide (Jacobson and Ney, *Ber.*, 1889, **22**, 907) and methyl iodide (1:1.5) were heated in a sealed tube for 24 hours. The salt crystallised from water in colorless needles, m.p. 247°, yield 78%. (Found: I, 41.58.  $C_{10}H_{12}NIS$  requires I, 41.64 per cent).

**2-*p*-Diethylaminostyryl-6-methylbenzothiazole methiodide.**—2:6-Dimethylbenzothiazole methiodide (0.305 g.), *p*-diethylaminobenzaldehyde (0.177 g.), absolute alcohol (5 c.c.) and

piperidine (2 drops) were refluxed for 6 hours. The dye crystallised out next day and was recrystallised from methyl alcohol in needles with a strong bottle-green reflex. yield 32%. (Found: N, 6.00; I, 27.29.  $C_{21}H_{25}N_2IS$  requires N, 6.04; I, 27.37 per cent).

*2:4:6-Trimethylbenzothiazole methiodide.*—2:4:6-Trimethylbenzothiazole, prepared from thioaceto-*m*-xylidide (Jacobson and Ney, *loc. cit.*), and methyl iodide (1:1.5) were heated in a sealed tube for 24 hours. The salt was recrystallised from water in long colorless needles, m.p. 227-28°, yield 78%. (Found: I, 39.65.  $C_{11}H_{14}NIS$  requires I, 39.81 per cent).

*2-p-Diethylaminostyryl-4:6-dimethylbenzothiazole methiodide.*—2:4:6-Trimethylbenzothiazole methiodide (0.16 g.), *p*-diethylaminobenzaldehyde (0.089 g.), absolute alcohol (5 c.c.) and piperidine (2 drops) were refluxed for 2 hours. The dye which crystallised out was recrystallised from methyl alcohol in needles with a yellow reflex, yield 38%. (Found: N, 5.80; I, 26.39.  $C_{22}H_{27}N_2IS$  requires N, 5.86; I, 26.57 per cent).

One of us (J.C.B.) gratefully records his thanks to the authorities of the Patna University for the grant of a research scholarship to him during a part of the pendency of the work.

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## DURABILITY OF SODA—LIME—SILICATE GLASSES. PART III. RELATION BETWEEN ANNEALING AND CHEMICAL DURABILITY

BY AJITENDU SEN, AMALENDRA CHOWDHURY AND H. N. DAS-GUPTA

The net effect of annealing on chemical durability of glass in bulk and the changes of chemical durability, when chilled glass is subjected to different temperatures for a specified period and to a definite temperature for varying periods, have been studied. Findings of Williams and Weyl have been verified by studying the effect of heat treatment on the surface durability.

The annealing of glass is a problem of profound practical importance and different investigations have contributed substantially towards its different aspects. Thus, some workers were interested in introducing suitable optical methods for detection and measurement of strain (Sir David Brewster, *Phil. Trans.*, 1814, 1815, 1816; Wilson, *J. Soc. Glass Tech.*, 1919, **3**, 256; English, *ibid.*, 1919, **3**, 258; Twyman, *ibid.*, 1917, **1**, 67). The rate at which strain is removed from glass has been the subject of several studies (Preston, *Glass Ind.*, 1934, **15**, 57; Littleton, *Ind. Eng. Chem.*, 1933, **25**, 748; Baily and Sharp, *J. Amer. Ceram. Soc.*, 1933, **16**, 367; Lillie, *ibid.*, 1936, **19**, 45). Again a considerable amount of research work has been carried out of late years upon the relationship between the composition of a glass and its annealing temperature (English and Turner, *J. Soc. Glass Tech.*, 1918, **2**, 90; 1919, **3**, 278; 1920, **4**, 387, 1921, **5**, 115, 357; 1923, **7**, 25, 73; 1924, **8**, 173; Adams and Williamson, *J. Franklin Inst.*, 1920, **190**, 597, 835; Valasek, U.S.A. Bureau of Standards, 1920, No. 358; Weidert, *Sprechsual*, 1921, **54**, 423; *Glashutte*, 1921, **51**, 789, 803, 820; 1922, **52**, 1, 17). Also, several investigators have shown that physical properties like density, coefficient of thermal expansion, specific heat, electrical properties, etc., are considerably modified as a result of annealing of glass (English and Turner, *J. Soc. Glass Tech.*, 1920, **4**, 153; Tool and Eichlin, *J. Optical Soc. Am.*, 1924, **8**, 419; *J. Amer. Ceram. Soc.*, 1925, **8**, 1; Tool and Hill, *J. Soc. Glass Tech.*, 1925, **9**, 185; Peters, Bureau of Standards, Scientific papers, 1926, No. 521; Wulff and Mazumdar, *Z. physikal. Chem.*, 1936, **31B**, 319; Callender, *Trans. Roy. Soc.*, 1887, **A**, **178**, 161; Holborn and Gruncisen, *Ann. Physik*, 1901, **6**, 136; Turner and Winks, *J. Soc. Glass Tech.*, 1930, **14**, 84).

Previous works, relating to the influence of heat treatment on chemical durability of glass, reveal that Keeppeler (*Glasstech. Ber.*, 1927, **5**, 97) was the first to point out the sharp distinction in respect of chemical resistivity between the surface of glass and its bulk. It was also pointed out that annealing not only removed mechanical stress, but that it also changed the constitution of glass. Similar work is that of Williams and Weyl (*Glass Ind.*, 1945, **26**, 275, 325). In accordance with their findings the following changes are effected in glass, which has been subjected to annealing process: (i) Increased concentration of alkali at the surface, (ii) structural change, causing strengthening of the bond between the alkali ion and the anionic network, and (iii) removal of alkali from the surface by volatilisation and by its reaction with furnace gases.

The present work was undertaken with threefold objects : Firstly, to study the net effect of annealing on chemical durability of glass in bulk. Secondly, to make a systematic study of the change of chemical durability when a specimen of chilled glass is subjected to different temperatures for a specified period and to a definite temperature for varying periods. Thirdly, to find out the effect of heat treatment on surface durability and thereby to verify the findings of Williams and Weyl (*loc. cit.*) in respect of alkali concentration at the surface.

It will be seen in the experimental portion that annealing substantially contributes towards increased durability of the glass in bulk and that there is an optimum temperature for each composition at which the maximum effect is obtained (Tables I, III & VII). It is, however, very doubtful if this increased durability is due mainly to a structural change, which is expected to strengthen the bond between the alkali ion and the anionic network. The tendency of the alkali to migrate to the surface appears to be more even during annealing temperature range, provided the total surface area be large. Thus, under identical annealing temperature, the same glass gives divergent sulphuric acid values according as the glass is in the powdered or in the lump form. This will be evident from Table X. It has also been found that glass powder, which has been completely washed free of alkali, be successively subjected to heat treatments, concentration of alkali at the surface in decreasing order is found to take place on each occasion. This continues for a number of times and ultimately ceases. But this aspect of the problem will form the subject matter of a subsequent communication.

As on previous occasions, the determination of the durability of glass was made by taking recourse to powder test (Faraday, *Phil. Trans.*, 1830, p. 49; Plouze, *Compt. rend.*, 1856, **43**, 117; Mylius and Foerster, *Ber.*, 1889, **22**, 1092; *Z. Instrum.*, 1889, **9**, 120; Hagmaier, *Met. Chem. Eng.*, 1917, **16**, 604; Nicolardot, *Compt. rend.*, 1919, **169**, 335; Peddle, *J. Soc. Glass. Tech.*, 1920, **4**, 3, 299; 1921, **5**, 72, 195).

#### EXPERIMENTAL

In order to test the net effect of annealing on durability of glass in bulk, bottles, both annealed and unannealed and prepared from the same melt, were procured from two different manufacturing firms. These bottles were subjected to powder test in the usual way. Table I embraces the results obtained with such bottles and Table II gives a complete analysis of unannealed specimen No. 2.

TABLE I

Source	Type of glass.	Sulphuric acid values.	
		Unannealed.	Annealed.
Bharat Glass Works	Soda-lime-silicate	(i) 837	721
		(ii) 835	721
Glass Products Ltd.	Soda-lime-boro silicate, No. 1	(i) 595	556
		(ii) 597	557
Do	soda-lime-boro- silicate, No. 2	(i) 535	462
		(ii) 536	462

It will be evident from Table I that annealing increases durability to a considerable extent.

TABLE II

Component	SiO <sub>2</sub>	R <sub>2</sub> O <sub>3</sub>	CaO	B <sub>2</sub> O <sub>3</sub>	Alkali*
% Composition	71.35	3.50	5.90	1.30	17.95

(Total 100)

\*By difference.

With a view to studying the effect of varying temperatures on durability of glass, maintaining the duration of exposure constant, the unannealed specimen No.2 was broken into lumps of suitable sizes. About 20 g. of the broken lumps were taken for every experiment, each being done under identical conditions. The exposures to temperatures, varying between 100° and 700°, were given in an electrically heated muffle furnace, the temperature of which could be regulated properly. In each case, the furnace was raised to the desired temperature and then the charge was introduced in a platinum basin, the temperature maintained constant for 3 hours, and then allowed to fall slowly. As the furnace was properly insulated, the fall in temperature was a gradual one and required a period of 18 hours to attain room temperature. Up to 500° there was no deformity of the glass mass, but there was appreciable deformity, followed by fusion, at temperatures above 600°. After exposure, each batch was subjected to powder test and the results of such tests have been included in Table III.

TABLE III

Temp.	Exposed for	H <sub>2</sub> SO <sub>4</sub> value.	Temp.	Exposed for	H <sub>2</sub> SO <sub>4</sub> value.
Atmospheric (28°)	—	535	600	3 hrs	(1) 425
100°	3 hrs.	512			(2) 426
200°	3	495			(3) 425
300°	3	485	700	3	(1) 580
400°	3	481			(2) 579
500	3	470			(3) 578

Table III shows that the sulphuric acid value gradually diminishes with the increase in temperature, attains a minimum value at 600°, and again increases as the temperature is further raised.

For obvious reason it was not possible to expose soda-lime-silicate glass to a temperature of 600° for annealing purpose. Naturally, to study the effect of time glass lumps were exposed to 500° for varying interval of time and the results of such treatments have been included in Table IV.

TABLE IV

Temp. = 500°.

Time (hrs.)	..	1	2	3	4	5	6	7	8	9
H <sub>2</sub> SO <sub>4</sub> value	..	482	477	470	456	435	427	425	425	425

Since in every case the rate of cooling was maintained constant, it appears from Table IV that for imparting maximum durability to a glass of fixed composition, the

duration of exposure should preferably be increased. The results of Table IV have been represented graphically in Fig. 1.

In order to corroborate further the observed effect of annealing, two new glasses of different compositions were melted and plained in different Morgan crucibles. Immediately after plaining they were withdrawn from the furnace so as to cool very rapidly. These specimens were next subjected to heat treatment. Table V shows the purity of the raw materials used, Table VI the percentage batch composition, and Table VII shows the effect of annealing at different temperatures.

FIG. 1

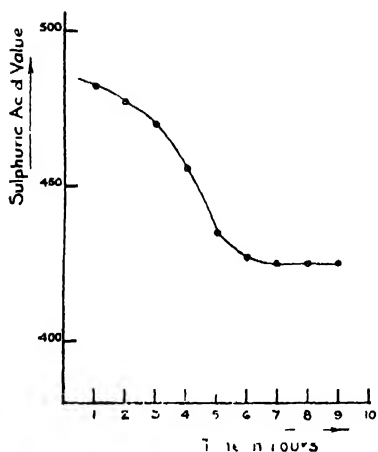


FIG. 2

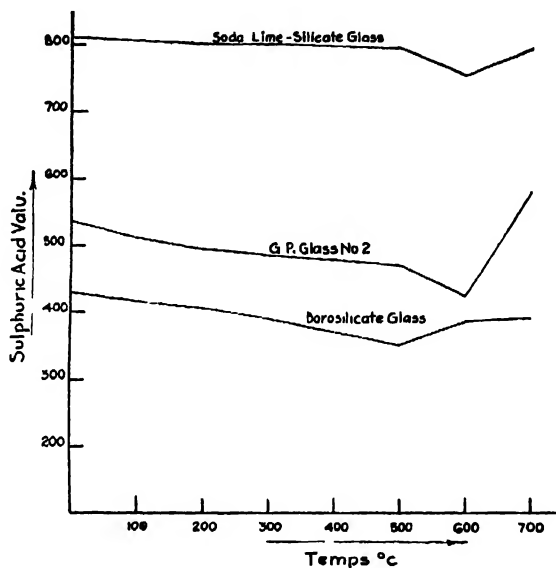


TABLE V

Material	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO.	MgO	Na <sub>2</sub> O.	B <sub>2</sub> O <sub>3</sub>	Loss.
Sand	97.2%	0.3%	1.8%	0.4%	Trace	—	—	0.3%
Lime	1.9	0.8	2.66	71.0	Trace	—	—	23.2
Soda ash	0.29	Nil	—	S. trace	S. trace	18.76%	—	10.2
Borax	0.08	Nil	S. trace	S. trace	S. trace	15.89	36.06	47.5 (as water)

TABLE VI

Batch No	% Composition			
	SiO <sub>2</sub>	CaO.	Na <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>
a	73	9	18	—
	65	9.5	17.5	8.0

TABLE VII

Temp.	Duration.	Sulphuric acid value of batch	
		a.	b.
Ordinary (28°)	—	815	427
100°	3 hrs.	805	415
200°	3	800	405
300°	3	800	390
500°	3	795	351
600°	3	756	388
700°	3	795	390

If, however, a specimen of glass be brought to a desired temperature from a higher one, kept at that for 3 hours and then allowed to cool, the sulphuric acid value of the specimen is invariably slightly higher than that recorded previously. This will be clear from Table VIII, where each of the specimen was first raised to 700° and then brought to a particular temperature for usual annealing. For the sake of comparison the values obtained by direct heat treatment have also been incorporated in the table.

TABLE VIII

Duration 3 hours.

H <sub>2</sub> SO <sub>4</sub> value by heat treatment					H <sub>2</sub> SO <sub>4</sub> value by heat treatment				
Batch No.	Temp.	Duration.	Direct.	Indirect.	Batch No.	Temp.	Duration.	Direct.	Indirect.
a	300°		800	810		300°		390	410
	500°	3 hrs.	795	800		500°	3 hrs.	351	380
	600°		756	770	b	600°		388	395
	700°		795			700°		390	

Fig. 2 gives a graphic representation of the data included in Tables I, III and VII.

To study the effect of heat treatment on surface durability, bottles of almost identical shape and capacity and prepared from the same melt, were procured from the previously mentioned firms. Each set comprised one annealed and one unannealed bottle. Each was filled with a definite volume of water and kept suspended in a water-bath, the level of water, both inside and outside the bottles, was maintained constant. The temperature of the water-bath was gradually raised to boiling and maintained at that for three hours. The whole was allowed to attain the room temperature slowly. Content of each bottle was taken in a previously treated conical flask and titrated with *N*/50-sulphuric acid. These results have been included in Table IX.

TABLE VIII

Source of glass bottle.	H <sub>2</sub> SO <sub>4</sub> required to neutralise the extract from	
	unannealed glass.	annealed glass.
Bharat glass Works	44.5 mg.	66.7 mg.
Glass Products Ltd.	5.0	7.5

The results shown in Table IX are in close agreement with the findings of Williams and Weyl (*loc. cit.*). But it is sufficiently clear that the tendency of alkali to migrate to the sur-

face is relatively high in soda-lime-silicate glass. As pointed out previously, the effect of constitutional changes during annealing appears to be less marked when the total surface area of the same glass is increased indefinitely. Thus, it will be seen from Table X that the net sulphuric acid value of the same glass is different according as the specimen is annealed in the lump or in the powdered form. The glass was powdered to pass 160 mesh sieve.

TABLE X

Batch No.	Annealing temp.	Duration.	H <sub>2</sub> SO <sub>4</sub> value	
			Lump.	Powdered.
a	500°	3 hrs.	795	885
b	500°	3	351	373

Grateful thanks of the authors are due to Mr. M. L. Sen Gupta, Chief Chemist, Messrs Glass Products Ltd., and to Messrs The Bharat Glass Works, for their supply of bottles of all descriptions.

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## THE EFFECT OF METALS ON POLYMERIZATION

BY JOYTIRINDRA NATH SEN, RANAJIT SEN GUPTA AND SANTI R. PALIT

The effect of oleates of Mn, Fe, Co, Ni, Cu, Zn on the peroxide-catalysed polymerization of styrene and methyl methacrylate in solution in toluene and *n*-butyl alcohol has been studied. Copper is found to inhibit the polymerization of styrene and strongly retard the polymerization of methyl methacrylate. All other metals have a small retarding effect which is generally more prominent in *n*-butyl alcohol than in toluene. Iron (ic), however, accelerates styrene polymerization.

The effect of metals and metallic compounds on polymerization has been but little investigated in a systematic manner. Such a study, however, is of interest as metals are used for fabrication of reaction kettles and also as metals are known to have a strong influence on many well known chemical reactions. The purpose of the present work is to investigate the influence of different metals on polymerization reactions. Mention is, however, frequently made in the patent literature on the influence of sodium and alkali metal compounds on butadiene, isoprene, etc., and on the use of metallic powder and container in connection with monomers, specially those connected with synthetic rubber industry (Burk, Thompson, Weith, Williams, "Polymerization", 1937, Chap. III; British Patents, 504; 734; vide Fleck, "Plastics Manual", 1947, p. 17).

As metals as such are insoluble, we have chosen suitable metallic compounds viz., oleates which are soluble in organic solvents. We have studied the following metals viz., Mn, Fe, Co, Ni, Cu and Zn; these were chosen as they are the active transitional elements used as catalysts and also are the most common materials of construction for reaction kettles. We have limited ourselves to two monomers, styrene and methyl methacrylate, and studied them in solution in toluene and *n*-butyl alcohol (monomer : solvent = 1 : 6.5 by volume, approx.).

### EXPERIMENTAL

**Monomers.**—Commercial styrene was purified by washing successively with alkali, water, etc., and distilling in *vacuo*. Methyl methacrylate was prepared by the depolymerization of commercial polymethyl methacrylate. This was washed as usual with dilute alkali and water, etc. and distilled carefully twice under a 16" vigreux type of column.

**Solvents.**—Baker's C.P. variety toluene was used as such. Laboratory reagent quality (B.D.H.) of *n*-butyl alcohol was distilled over drierite (CaSO<sub>4</sub>) before use.

**Metallic Soaps.**—The metallic oleates were prepared by the usual method of double decomposition between dilute solutions of sodium oleate and slight excess of the metallic salts. These were washed several times with water until free from inorganic impurities, dried in a vacuum oven at 50°, and used as such without further purification. The metal content of the soaps was determined by standard methods of analysis.

**Catalyst.**—Benzoyl peroxide was prepared by the method of Gambarjan, (*Ber.*, 1909, 42, 4008). The product was crystallised twice from aqueous alcohol and dried at ordinary temperature. The sample was assayed iodometrically by standard method.

**Polymerization.**—Freshly distilled monomer, solvent, and solutions of catalyst and soap were mixed in suitable proportions and 5 c.c. of the mixture pipetted into dry 16 mm. pyrex test tubes with constrictions near the middle, which were previously washed successively with hot chromic acid, sulphurous acid, water, etc. The contents were frozen in liquid oxygen and sealed under vacuum at the constriction.

The ampoules containing the reaction mixture were then placed in a thermostat maintained at  $80^{\circ} \pm 0.1^{\circ}$ . After desired intervals of time ampoules were taken out and the amount of polymer formed was estimated gravimetrically after isolation. The polymer was precipitated from solution by adding an excess of methyl alcohol containing some hydrochloric acid (to decompose the soap). Unconverted monomer, catalyst and soap were removed with the alcohol and the precipitate was dissolved in benzene, reprecipitated with methyl alcohol, and dried in a vacuum oven at 50 before weighing.

**Viscosity.**—Viscosity of the samples of polymer was measured with an Ostwald type of viscometer of efflux time of about 180 sec. with acetone. The temperature was kept constant within  $\pm 0.005^{\circ}$ . Intrinsic viscosity,  $[\eta]$ , was evaluated from an extrapolation of the plot of  $\eta_{sp}/c$  versus  $c$ , where  $c$  is concentration expressed in g. per 100 c.c. of solution, *i.e.*

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c}$$

Our results are presented below with reference to each soap separately. In some cases the full course of polymerization was not followed and data for only three hours' time are presented. For comparison we have generally utilised the yield for this period of polymerization time unless otherwise stated. The accuracy and reproducibility of the yield data are generally within one unit per cent and hence any effect within this limit or below 5% of the yield in the control experiment is designated as small. In order to obtain the effects under identical conditions, each experiment with metallic soap is accompanied by a separate control experiment without the added soap right through under exactly the same conditions.

### Manganese

The results with manganese are presented in Table I; they are graphically represented in Fig. 1 and summarised below.

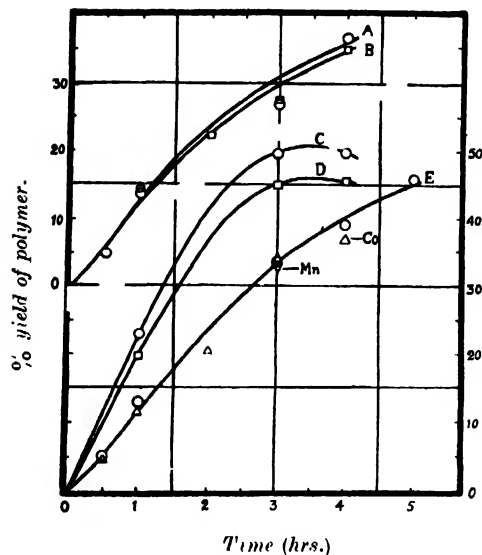
(a) *Toluene as solvent.*—For styrene there is a slight but definite retardation. Methyl methacrylate also suffers a small fall in yield.

(b) *n-Butyl alcohol as solvent.*—In this solvent the retarding influence is more magnified. Polymerization of styrene is retarded by about 38% and that of methyl methacrylate by about 33.5%.

It is to be noted that manganese retards polymerization of both the monomers to the same extent, being very small, if at all, in toluene and being quite high (about one-third decrease) in *n*-butyl alcohol. This magnification of the effect in *n*-butyl alcohol, as will be observed later, is a common feature of almost all cases we have studied.

FIG. 1

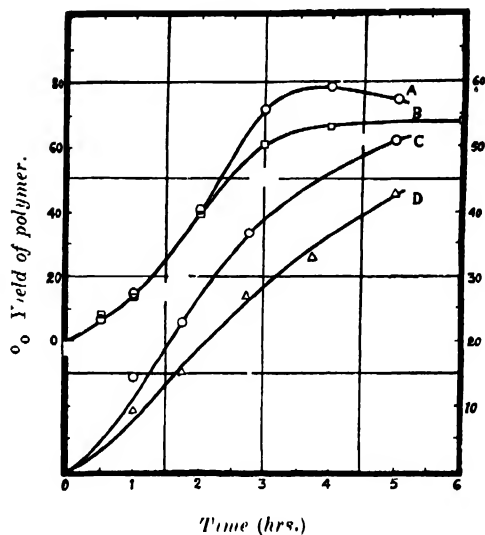
Effect of metallic soaps on methyl methacrylate polymerization.



Curve A—Control for B. B—Mn oleate additive. E—Control for C. C—Co oleate additive. (Toluene solvent for A, B, C and E). C'—Control for D and Mn. D—Ni oleate additive. Mn—Mn oleate additive (single point). (*n*-Butyl alcohol solvent for C', D and Mn).

FIG. 2

Effect of ferric oleate on methacrylate polymerization.



Curve A—Control for B. B—Ferric oleate additive (0.85%) (*n*-Butyl alcohol solvent for A and B). C—Control for D. D—Ferric oleate additive (2.1%) (Toluene solvent for C and D).

### Iron

Data are presented in Table II and graphically represented in Fig. 2. The results are as follows:

(a) *Toluene as solvent.*—Iron has a slight accelerating tendency in the polymerization of styrene. In this solvent the effect is, however, very small. Methyl methacrylate polymerization is retarded to the extent of about 27%.

(b) **n*-Butyl alcohol as solvent.*—The accelerating influence of iron on styrene is much augmented in this solvent, the yield being raised by 19%. Methyl methacrylate polymerization is, however, retarded to an extent of about 15%.

It will be observed that iron retards the polymerization of methyl methacrylate but accelerates the polymerization of styrene, and as usual, the effect is magnified in *n*-butyl alcohol. This shows that the effect of the additive is possibly to influence one of the vital polymerization steps e.g., the chain propagation or termination step and not a simple effect on the peroxide decomposition. It may be noted from Fig. 2 that the retardation in toluene is present as usual throughout the course of the polymerization, whereas in *n*-butyl alcohol, though of course with half the amount of iron present, the retardation is perceptible only after about 40% conversion.

**Cobalt:** (a) *Toluene as solvent*.—As will be seen from Table III and Fig. 1, cobalt exerts very little influence, if at all, on the polymerization of styrene and methyl methacrylate.

#### Nickel

Data are presented in Table IV and graphically represented in Fig. 1. They are summarised below.

(a) *Toluene as solvent*.—Nickel has very small influence on styrene as well as methyl methacrylate polymerization. The variation between control and experiment is rather small and so does not warrant any positive conclusion.

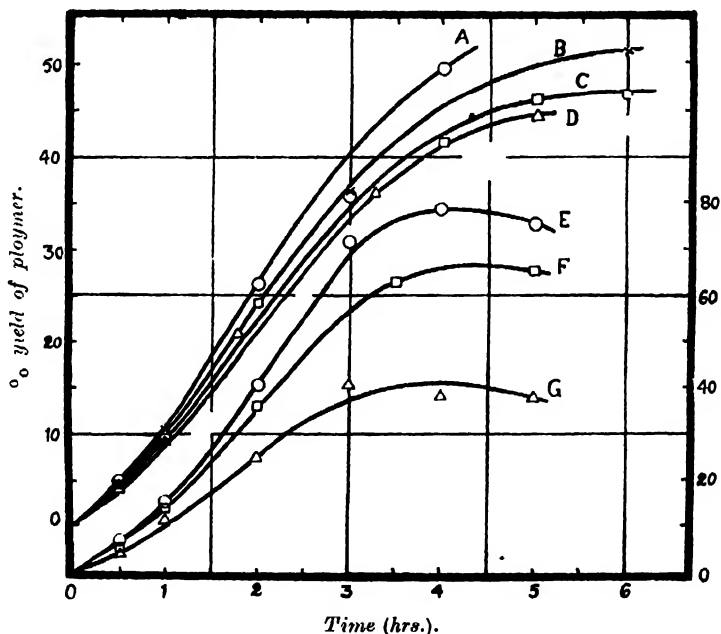
(b) *n-Butyl alcohol as solvent*.—As will be seen in Fig. 1, retardation, though feeble, is much more marked here. For styrene it is 7.5% and for methyl methacrylate the value is about 12%.

#### Copper

Data are presented in Table V and some are represented graphically in Fig. 3 and Fig. 4.

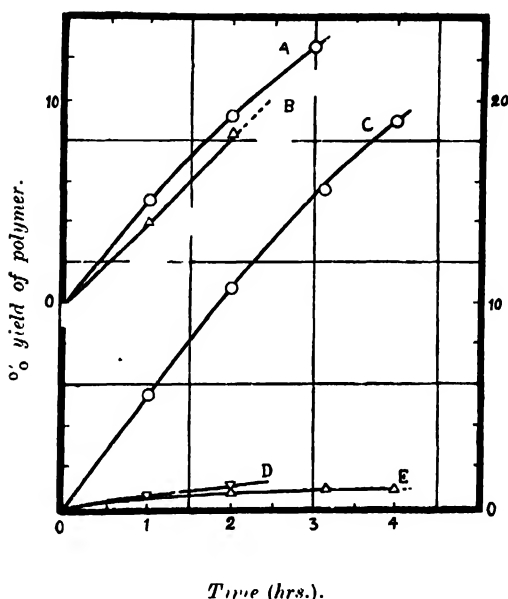
(a) *Toluene as solvent*.—Copper exerts a profound influence on styrene polymerization. As will be seen from Fig. 4 there is an almost complete suppression of reaction as is evidenced by the magnitude of the fall in yield, which is about 95 per cent. For methyl methacrylate (Fig. 3), however, retardation is not so marked, being only of the order of 18%.

FIG. 3  
Effect of copper oleate on methyl methacrylate polymerization.



Curve A—Control for B, C and D. B—Copper oleate additive (0.46%). C—Copper oleate additive (1.14%). D—Copper oleate additive (2.28%). (Toluene solvent for A, B, C and D). E—Control for F and G. F—Copper oleate additive (1.0%). G—Copper oleate additive (2.0%). (n-Butyl alcohol solvent for E, F and G).

FIG. 4

*Effect of metallic oleates on styrene polymerization.*

Curve A—Control for B. B—Zinc oleate additive (2.0%). [*n*-Butyl alcohol and toluene mixture (1; 1.4 by volume) solvent for A and B]. C—Control for D and E. D—Copper oleate additive (1.0%). E—Copper oleate additive (2.0%). (Toluene solvent for C, D and E)

(b) *n*-Butyl alcohol as solvent.—The strong inhibition for styrene in toluene solution is also maintained in this solvent. Methyl methacrylate is also retarded to a greater extent in this solvent (Fig. 3), the fall in yield being 45.8%.

In order to ascertain the effect of this strong retardation by copper on the molecular weight of the polymer formed, an experiment was conducted with 1/16 of the weight of peroxide catalyst as given in Table V. This reduced the speed of polymerization to 1/4 of former value at the initial stages, and two samples (one control and one with 2% copper oleate) were isolated after 13 hours of polymerization. The control had a yield of 56.5%, whereas with copper the yield was reduced to 36%. The intrinsic viscosity,  $[\eta]$ , of the two samples in benzene solution are 0.85 and 0.62 respectively. It will be observed that the  $[\eta]$  decreases by over 27% by using copper as retarder. This probably signifies that the retardation is brought about by some interference with the termination process and not probably by reducing the rate of initiation. In this retarded reaction the rate decreased more than the molecular weight and this agrees with Cohen's observation on retarded reactions in general (Cohen, *J. Amer. Chem. Soc.*, 1947, **69**, 1057). This again points to the possibility of copper playing some vital part in deactivating the active centres in the chain growth process (Foord, *J. Chem. Soc.*, 1940, 48). Difficulty, however, remains as regards the nature of the chemical metamorphosis undergone by copper oleate

TABLE I

*Effect of manganese oleate on polymerization rate at 80°.*

Monomer.	Solvent.	Catalyst conc. (g. benzoyl peroxide per 100 g. monomer).	Additive conc. (g./100c.c. soln.)	Time (hours).	Yield.	%Retardation. (3 hours)
Methyl methacrylate	Toluene	0.98	Nil	$\frac{1}{2}$	47.0%	
				1	13.6	
				3	26.6	
				4	36.4	
		2.5		1	14.5	Small
				2	22.2	
				3	27.2	
				4	34.7	
	<i>n</i> -Butyl alcohol	0.91	Nil	1	22.8	
				3	49.6	
				4	49.6	
		2.0		3	33.0	33.5
	Styrene	0.96	Nil	3	15.8	
			2.0	3	15.1	Small
	<i>n</i> -Butyl alcohol	0.96	Nil	3	14.7	
			2.0	3	9.1	38.1

TABLE II

*Effect of ferric oleate on polymerization rate at 80°.*

Monomer.	Solvent.	Catalyst (g. benzoyl peroxide per 100 g. monomer).	Additive conc. (g/100c.c. soln.).	Time (hours).	Yield.	%Retardation. (3 hours).
Methyl methacrylate	Toluene	0.98	Nil	1	14.6%	
				$1\frac{1}{2}$	22.9	
				$2\frac{1}{2}$	36.7	
				5	51.0	
		2.1		1	9.0	26.9
				$1\frac{1}{2}$	15.3	
				$2\frac{1}{2}$	27.3	
				$3\frac{3}{4}$	32.9	
				5	43.2	
	<i>n</i> -Butyl alcohol	0.98	Nil	$\frac{1}{2}$	6.7	
				1	14.4	
				2	40.7	
				3	71.9	
				4	78.4	
		0.85		5	74.8	
				$\frac{1}{2}$	8.7	15.2
				1	13.6	
				2	39.4	
				3	61.0	
				4	65.5	
				6	68.7	
Styrene	Toluene	0.96	Nil	3	15.8	
			2.0	3	16.4	Small (acceleration)
	<i>n</i> -Butyl alcohol	0.96	Nil	3	14.7	
			0.8	3	17.5	19 (acceleration)

TABLE III

*Effect of cobalt oleate on polymerization rate at 80°.*

Monomer.	Solvent.	Catalyst (g. benzoyl peroxide per 100 g. monomer).	Additive conc. (g/100c.c. soln.).	Time (hours).	Yield.	%Retardation (3 hours).
Methyl methacrylate	Toluene	0.98	Nil	$\frac{1}{2}$	4.9 %	
				1	13.0	
				3	33.5	
				4	39.1	
				5	46.0	
		0.91	2.5	$\frac{1}{2}$	4.6	Small
				1	11.5	
				2	20.5	
				3	34.3	
				4	36.9	
Styrene	Toluene	0.96	Nil	3	33.6	
			2.0	3	33.2	Small
		0.96	Nil	3	15.8	
			2.0	3	15.5	Small

TABLE IV

*Effect of nickel oleate on polymerization rate at 80°.*

Monomer.	Solvent.	Catalyst (g. benzoyl peroxide per 100 g. monomer).	Additive conc. (g./100c.c. soln.).	Time (hours).	Yield.	%Retardation. (3 hours)
Methyl methacrylate	Toluene	0.91	Nil	3	33.6 %	
			1.4	3	35.1	Small
	<i>n</i> -Butyl alcohol	0.91	Nil	1	22.8	
				3	49.6	
		0.96	1.5	4	49.6	
				1	19.8	12.3
Styrene	Toluene	0.96	Nil	3	45.0	
			1.4	3	45.8	
			1.5	4	45.8	
	<i>n</i> -Butyl alcohol	0.96	Nil	3	15.8	
			1.4	3	15.1	Small
			1.5	3	14.7	
				3	13.6	7.5

which is apparently not a reduced form of copper, neither is it found in a combined state in the polymer, though such combination for benzoquinone was observed by Breitenbach, Springer and Horeischy (*Ber.*, 1938, **71**, 1438).

Reduction of soap concentration, as will be seen from the above figures, generally decreases the extent of retardation or inhibition.

TABLE V

*Effect of copper oleate on polymerization rate at 80°*

Monomer	Solvent	Catalyst (g. benzoyl per oxide per 100 g monomer).	Additive conc. (g/100c.c. soln.).	Time (hours)	Yield	% Retardation. (3 hours).
Methyl methacrylate	Toluene	0.98	Nil	$\frac{1}{2}$	4.9%	
				1	9.9	
				2	26.6	
				3	35.8	
				4	48.9	
		2.28		$\frac{1}{2}$	4.4	18.4
				1	8.9	
				$1\frac{1}{2}$	21.3	
				$3\frac{1}{2}$	36.3	
				5	44.4	
		1.14		$\frac{1}{2}$	4.0	15.2
				1	9.8	
				2	24.1	
				4	41.9	
				5	46.6	
				6	46.1	
	<i>n</i> -Butyl alcohol	0.46	0.46	$\frac{1}{2}$	4.5	9.1
				1	10.9	
				3	36.2	
				6	51.4	
		Nil	Nil	(vide Table II)		45.8
				2.0		
				$\frac{1}{2}$	3.6	
				1	11.5	
				2	24.8	
				3	40.5	
				4	38.0	
				5	37.8	
		1.0		$\frac{1}{2}$	4.9	17.6
				1	13.9	
				2	36.7	
				$3\frac{1}{2}$	62.7	
				5	65.2	
		0.96	Nil	6	47.5	
				13	56.5	
				2.0		
				6	11.4	75.9 (6 hrs.)
				13	36.0	36.5 (13 hrs.)
Styrene	Toluene	0.96	Nil	3	15.8	
				2.0	0.7	95.4
				Nil		
				1	5.6	
				2	10.8	
		2.0		$3\frac{1}{2}$	15.6	
				4	19.0	
				2	0.78	94.8
				$3\frac{1}{2}$	0.9	
				4	0.9	
	<i>n</i> -Butyl alcohol	0.96	Nil	1.0	0.5	90.7
				2	1.0	
				3	14.7	
				2.0	1.7	88.2



TABLE VI

*Effect of zinc oleate on polymerization rate at 80°.*

Monomer.	Solvent.	Catalyst (g. benzoyl per- oxide per 100 g. monomer).	Additive conc. (g/100c.c. soln.).	Time (hours).	Yield.	% Retardation. (1 hour)
Methyl methacrylate	Toluene	0.91	Nil	3	33.6 %	
			1.6	3	34.1	Small
	<i>n</i> -Butyl alcohol	0.91	Nil	3	49.6	
			0.38	3	47.1	5.2
Styrene	Toluene	0.96	Nil	3	15.8	
			1.6	3	15.8	Small
	<i>n</i> -Butyl alcohol	0.96	Nil	3	14.7	
			0.38	3	11.2	23.3
	<i>n</i> -Butyl alcohol + toluene (1:1.4 by vol.)	0.96	Nil	1	5.0	
				2	9.2	
				3	12.6	
			2.0	1	3.9	21.7 (1 hrs)
				2	8.3	9.8 (2 hrs.)

*Zinc*

Data are presented in Table VI.

(a) *Toluene as solvent.*—Zinc exerts no appreciable effect on the rate of polymerization of methyl methacrylate or styrene.

(b) *n-Butyl alcohol as solvent.*—Styrene polymerization is retarded to an extent of 23.3%, though for methyl methacrylate the retardation is small, being about 5%.

Since unlike all the metallic soaps studied, zinc oleate appeared to be only sparingly soluble in both toluene and *n*-butyl alcohol, it was thought that the lack of activity might be due to low concentration of zinc in solution. So an experiment was carried out in a toluene—*n*-butyl alcohol mixture in which zinc oleate is highly soluble. Styrene polymerization was retarded at the initial stages of reaction as will be seen from the upper pair of curves in Fig. 4.

## DISCUSSION

Though metals are generally observed to catalyze ordinary chemical reactions, we find that all the metallic soaps studied have a tendency to retard polymerization, the only exception being iron which produces a definite, though small, acceleration on styrene. The very small acceleration shown by nickel on methyl methacrylate in toluene solution is rather doubtful. The retardation by metallic soaps, though general, is in most cases very small. And in this respect copper stands out prominent from all the rest in producing a strong retardation or almost complete inhibition (Figs. 3 and 4). Our present state of knowledge about the mechanism of retardation and inhibition (Bartlett, Hammond, Kowart, *Trans. Faraday Soc.*, Discussion, 1947, 2, 342; Rohrs, Staudinger, Vieweg, "Fortschritte der Chemie, Physik und Technik der Makromolekularen Stoffe", Bd. II, 1942, pp. 36-48), is that the added

substances either destroy or combine with a growing radical forming a stable one incapable of participating in further propagation. Since the metals we have studied have the exceptional property of forming co-ordination complexes, it is not unexpected of them to combine with the free radicals formed in the reaction and thus produce the effects observed.

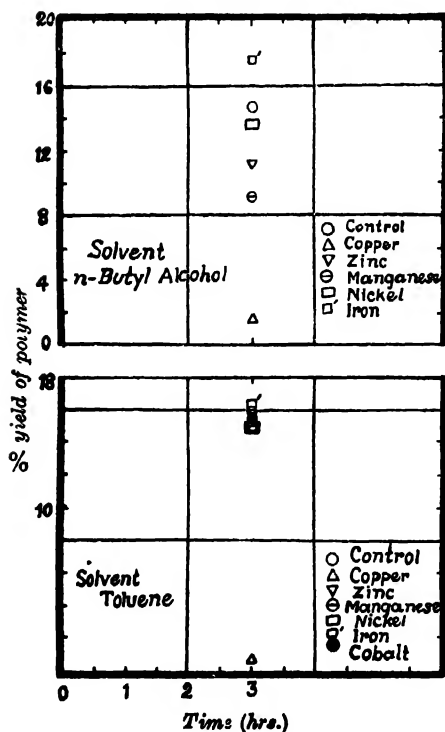
It is known that higher fatty acids, such as oleic acid, have very little or no influence on polymerization. Our observation that oleates of different metals do behave differently in their capacity to retard or accelerate polymerization and that the effect in some cases is negligibly small, points to the same conclusion. The activity of metallic soaps is therefore ascribed to the metallic part of the compound.

As regards the influence of solvents in our investigations, two significant features deserve mention :—

(a). The polymerization of methyl methacrylate is faster in *n*-butyl alcohol than in toluene, whereas that of styrene is only very little affected. From simple considerations it seems probable that the carbon-carbon double bond in methyl methacrylate is affected more by the alcoholic solvent than by toluene owing to hydrogen bond formation between

carbonyl oxygen and hydroxylic hydrogen, such as  $\text{C}=\text{C}-\text{O}\cdots\text{H}-\text{O}-\text{R}$ . This interaction possibly results in polarisation of the double bond and consequent diminution in the energy of activation of the reaction concerned. Such interaction between styrene and the solvents studied is precluded from similar considerations. The above observation is corroborated by our work in diethylene glycol medium where the rate of polymerization is even faster than in *n*-butyl alcohol (data not reported here).

Fig. 5.



(b). The effects produced by the metallic additives in *n*-butyl alcohol as solvent are generally much more prominent than in toluene. To visually illustrate this power of magnification of *n*-butyl alcohol a comparative plot of the data for styrene with different metallic soaps is furnished in Fig. 5. It will be observed that though the sequence is more or less the same within the limits of experimental error, the points for all metals except copper are crowded within a yield range of only one and a half per cent (between 15 to 16.5%) in toluene, whereas the same points get spread over a range of 9% (between 9 to 18% yield) in *n*-butyl alcohol, which makes it easier to assess their relative effect.

Determination of intrinsic viscosity  $[\eta]$  for different samples including those obtained from control as well as from the soap-retarded polymerization of the methyl methacrylate shows that  $[\eta]$  in acetone varies between 0.24 to 0.35. This shows that the

molecular weight of the polymer produced is rather small. It is also found from the viscosity data that  $[\eta]$  for samples obtained in *n*-butyl alcohol as solvent is as a rule greater than those of otherwise identical samples in toluene. The fact that polymer is insoluble in *n*-butyl alcohol but is soluble in toluene may have some bearing on this observation.

An examination of our data suggests that a grading of the metals could be made in respect of their efficiency in retarding polymerization. The relative efficiency of the metallic soaps in this direction for methyl methacrylate and styrene in the two solvents can be represented thus.

Toluene as solvent :-(1) methyl Methacrylate  
 $\text{Cu, Fe} \gg \text{Mn, Zn, Co.}$   
 (Ni accelerates?)

(2) Styrene  
 $\text{Cu} \gg \text{Ni} > \text{Mn, Zn, Co.}$   
 (Fe accelerates).

*n*-Butyl alcohol as solvent : -(1) methyl methacrylate  
 $\text{Cu} > \text{Mn, Fe} > \text{Zn, Ni}$

(2) Styrene  
 $\text{Cu} \gg \text{Mn, Zn} > \text{Ni}$   
 (Fe accelerates).

From the above series we find that copper stands foremost in its capacity to retard or inhibit polymerization of methyl methacrylate and styrene in both the solvents. Manganese also is somewhat effective and the rest retard polymerization in general, but the extent is small. Iron is conspicuous by its exceptional property of acceleration on styrene polymerization irrespective of the solvent. Examination of the order in which the metals occur in the series suggests that apart from the influence, of monomers the solvents have some role in determining the relative efficiency of a metal in influencing polymerization

Variations of the amount of soap added show clearly (Fig. 3) that the magnitude of retardation produced by additives is definitely dependent on their concentration. It is to be noted that on halving the concentration of copper oleate, which inhibits the polymerization of styrene, the extent of inhibition is reduced by a definite, though very small, amount (Fig. 4). Due to insufficient data at our disposal, no attempt at formulation of a quantitative relation is made in this direction.

Lastly, a peculiar feature observed in the polymerization of methyl methacrylate in *n*-butyl alcohol must be noted. Under the conditions of our experiment a tendency towards a fall in the overall yield is observed after about 80 % conversion in the control experiments (Figs. 2 and 3) which coincides with polymerization time of nearly 4 hours. This tendency is also noticeable in the retarded reactions with copper or iron (ic) oleate as additive and in these cases the so-called maxima in the yield-time curve is reached after the same period of reaction, though of course at a much lower conversion (Figs. 2 and 3). It should be noticed, however, that this downward tendency of the yield-time curve is much less in

the retarded experiments than in the control ones. From the above observations it seems likely that some oxidative degradation or depolymerization of the polymer formed under the conditions of experiment (high temperature and high peroxide concentration) is responsible for this effect. Also it seems probable that the depolymerization process is retarded by the metallic additives which accounts for the decreased downward slope in the curves for the retarded reactions. This retarding effect on the degradation is expected if the mechanism of degradation of polymethyl methacrylate is a reverse polymerization, being a chain reaction involving radicals, as has been shown by Grassie and Melville, (*Trans. Faraday Soc.*, Discussion, 1947, **2**, 378).

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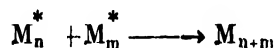
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## THE CHAIN TERMINATING STEP IN THE CATALYSED VINYL POLYMERIZATION

BY RANAJIT SEN GUPTA AND SANTI R. PALIT

A suggestion that the chain termination by catalyst fragments is a very important factor in deciding the molecular weights, overall rates etc., is made. An extreme case when only such termination occurs in a polymerization reaction is analysed theoretically and the size distribution function deduced. The consistency of such a hypothesis with previously observed data is shown.

In the common vinyl polymerizations, catalysed by peroxide type of catalysts, the generally accepted view is that the chain termination occurs by the mutual combination of two growing radicals, which for brevity we shall call combination termination process, as shown below.



where an asterisk indicates a free radical and M stands for a monomer unit. The main arguments are (cf. Herrington, *Trans. Faraday Soc.*, 1942, **40**, 236) :

- (1) The existence of a maxima in the size distribution curve of the polymer (Schulz, *Z. physikal. Chem.*, 1939, **43B**, 25, 49).
- (2) The slope of the overall velocity curve is proportional to the square root of the catalyst concentration.

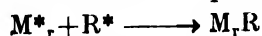
The bulk of the available data supports such a view, and the mechanism may be substantially correct.

In a previous communication (*communicated*) we demonstrated the enormous activity of potassium persulphate in solution polymerization of styrene in diethylene glycol. Our findings were that this catalyst was about 100 times more active than benzoyl peroxide in the same solvent and that the molecular weight of the product in the first instance was more than five to six times than in the latter case. These two facts appear at first sight to be mutually incongruent as the general view is that the faster the initiation, the smaller the molecular weight, as described by the following equation.

$$\text{Molecular weight (number average)} = \frac{\text{Velocity of propagation}}{\text{Velocity of termination}}$$

$$= \frac{\text{Velocity of propagation}}{\text{Velocity of initiation}}$$

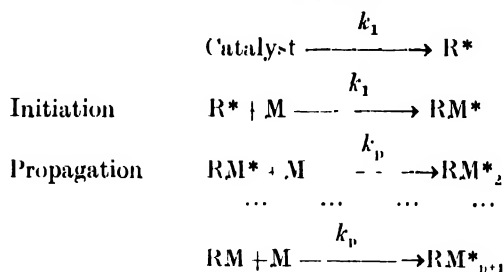
To meet this situation, a suggestion was made that the chain termination mechanism was not the same in the two cases. We assumed that in the case of peroxide-catalysed polymerizations there was a possibility that the termination might occur by the mutual collision of a free radical produced by the catalyst and the growing polymer chain (which we shall concisely term "the radical termination" process) as described by the equation,



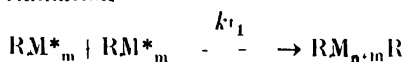
and that this mechanism did not play a very substantial part in the case of the persulphate.

The present communication is intended to analyse the effect of such a termination process on the overall rate and on the size distribution curve of the polymers formed.

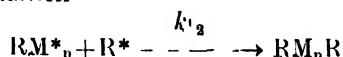
*The Kinetic Frame*



Termination : (a) Combination termination



(b) Radical termination



We are neglecting the chain transfer etc. which do not have any direct influence in our case.

In the above, we have supposed that the catalyst radical is deactivated in only two ways. This is, however, not the actual case and various side reactions occur by which the catalyst is decomposed. These side reactions, however, have no influence on the polymerization reactions except that they reduce the effective concentration of the catalyst. The common procedure is to introduce a "peroxide wastage factor" to make allowance for these side reactions (Nozaki and Bartlett, *J. Amer. Chem. Soc.*, 1946, **68**, 1686).

In all previous work,  $k_{t_1}$  was assumed to be equal to  $k_{t_2}$ , which no doubt simplifies the mathematics but tends to produce the impression that the "radical" termination process has no significant effect in the size distribution of the polymers formed. However,  $k_{t_1}$  cannot be equal to  $k_{t_2}$ , and this can at least be indicated in the case of solvents where the polymer is insoluble by following a simple argument as given below.

Evans and Baxendale (*Trans. Faraday Soc.*, 1947, **43**, 215) have shown that for such a system the chain termination may be essentially that of coagulation of colloidal solutions, as given by Smoluchowski and by modifying Somoluchowski's equation for such processes, he derives the equation,

$$k_t = \frac{8RT}{3000\eta} f(n)$$

$$\text{where } f(n) = \left[ 2 + \left( \frac{n_1}{n_2} \right)^{\frac{1}{3}} + \left( \frac{n_2}{n_1} \right)^{\frac{1}{3}} \right] / 4 \dots \dots \dots (1)$$

where  $n$  is the number of monomer units in the radicals taking part in termination.

In the case of usual combination termination we have average  $n_2$  virtually equal to  $n_1$  and hence  $f(n) \approx$  unity. However, in "radical" termination process this is far from the

case because for the production of polymers of molecular weight nearing 20,000,  $n_1:n_2$  is about 200 and hence

$$f_2(n) = \frac{2 + \left(\frac{200}{1}\right)^{\frac{1}{2}}}{4} + \left(\frac{1}{200}\right)^{\frac{1}{2}} \approx 2$$

and therefore  $\frac{k_2}{k_1}$  is of the order of two.

Here of course, we have made the rather questionable assumption that  $k_2$  can be calculated by equation (1), because the above equation has been deduced for the mutual coagulation of two colloidal particles, whereas in our calculation only one of the two fragments is insoluble and hence the equation is not strictly valid.

The possibility that the benzoate radical may also terminate (in addition to initiation) is very plausible. The recent observations of Mayo and Gregg (*J. Amer. Chem. Soc.*, 1948, **70**, 1284) indicate that any free radical can behave both as a catalyst and as an inhibitor and generally both concurrently depending upon conditions and in fact, the phenomenon of inhibition, which is only a limiting case of our radical termination, is shown by the above authors to run concurrently with initiation in the case of the triphenylmethyl radical and leads them to the conclusion that "the differences between them (initiation and inhibition) are quantitative rather than qualitative".

#### The Overall Rate

The consideration of only the combination termination process leads to the familiar equation (Evans, *Trans. Faraday Soc.*, 1947, Disc. **2**, 271)

$$-\frac{dM}{dt} = k_p \sqrt{\frac{k_1}{k_t}} c [M] \quad \dots \quad \dots \quad \dots \quad \dots \quad (2)$$

where  $M$  is the concentration of the monomer and  $k_1$ , the rate of decomposition of the catalyst concentrations. Redington (*J. Poly. Sci.*, 1948, **3**, 503) introduces a correction  $(1-w)$  to the catalyst concentration ( $w$  being the "peroxide wastage" factor) to explain his experimental results, and uses the modified equation,

$$-\frac{dM}{dt} = k_p \sqrt{\frac{(1-w)k_1}{k_t}} c [M] \quad \dots \quad \dots \quad \dots \quad \dots \quad (3)$$

We now consider the extreme case that the termination occurs exclusively by the 'radical' termination process. In this case assuming the usual steady state equations we proceed as follows: We have,

$$\frac{d[R]}{dt} = k_1 c - k_t [R][M] - k_2 [R][M] = 0$$

$$\text{and } \frac{d[M^*]}{dt} = k_1 [R][M] - k_1 [R][M^*] = 0$$

These two when solved gives,

$$[M^*] = \frac{k_1 [M]}{k_2} \text{ and } R = \frac{k_1 c}{2k_1 [M]}$$

And hence, the overall rate

$$\frac{d[M]}{dt} = -k_p [M^*][M] + k_1 [R][M]$$

$$k_p \frac{k_1}{k_2} [M]^2 + \frac{1}{2} k_1 c \quad \dots \quad \dots \quad \dots \quad (4)$$

[R and M\* being the catalyst fragment and the growing chains respectively].

The equation is true only if  $c \neq 0$ . This equation differs from the standard equation (equation 2) in the important respect that the rate is here linear with respect to the square of the monomer concentration instead of being proportional to its first power.

Schulz and his co-workers, (*Z. physikal. Chem.*, 1942, **51B**, 75; 1938, **39B**, 246) and Mark and Josefowitz (cf. Matheson, *J. Chem. Phys.*, 1945, **13**, 584) have shown the polymerization of methyl methacrylate, styrene, vinyl acetate and isoprene catalysed by benzoyl peroxide, or of styrene catalysed by tetraphenyl succinonitrite do not follow the simple equation (2) and can be expressed better by equation (5)

$$-\frac{d[M]}{dt} = \text{Const.} \times c^{\frac{1}{2}} [M] \left[ \frac{k[M]}{1+k[M]} \right]^{\frac{1}{2}} \quad \dots \quad \dots \quad \dots \quad (5)$$

where  $k$  is a constant.

To obtain this equation theoretically Schulz assumes that the monomer and the catalyst exist as an equilibrium-complex ( $k$  being the equilibrium constant) and that this complex rearranges unimolecularly to give the first radical unit of the growing chain



Similar views were expressed by Cuthbertson, Gee and Rideal (*Proc. Roy. Soc.*, 1939, **A**, 170, 300) to explain their results on the vinyl acetate polymerization. Matheson (*loc. cit.*) suggests an alternative explanation based on the rapidly reversible dissociation of the peroxide molecules within a cage of solvent molecules. However, it is interesting to note that the equation (5) which has a power  $> 1$  in  $M$  stands midway between equation (2) with power unity on  $M$  and equation (4) deduced by us with an exponent of 2 on  $M$ . Thus, a plausible explanation of the observed fact may be found in the simultaneous occurrence of the two termination process in actual reaction.



The results of Redington (*J. Poly. Sci.*, 1948, **3**, 503) reveal certain interesting features. He finds that lauryl, *p*-dichlorobenzoyl and 2-4 dichlorobenzoyl peroxide, though have greater rates of decomposition than benzoyl peroxide, initiate the polymerization to a much smaller extent, the results being that the overall yields of the polymers are smaller. This he explains successfully by introducing '*w*', the peroxide wastage factor as mentioned previously. The effect of *w* is to decrease the effective concentration of the catalyst *i.e.*, to decrease the effective value of  $k_1$  in equation (2). It is doubtful, however, if this simple explanation of Redington explains the whole picture because it can be easily shown that the ratio of the molecular weight averages of the polymers formed by the two catalysts may be given by

$$\frac{v_1}{v_2} = \sqrt{\frac{(1-w)[k_1]_2}{(1-w)[k_1]_1}} \quad \dots \quad \dots \quad \dots \quad (6)$$

Hence we might expect, the higher the  $(1-w)k_1$  value, the lower would be the molecular weight. However, exactly opposite occurs in the case of *p*-chlorobenzoyl peroxide, as shown in Table I, calculated from the data of Redington. (*loc. cit.*).

TABLE I

Temp.	Catalyst.	$k_1$ (hr <sup>-1</sup> )	<i>w</i> .	$(1-w)k_1$ .	Sp. viscosity.
100°	Benzoyl peroxide	1.65	0.08	1.52	1.94
	<i>p</i> -Chlorobenzoyl peroxide	1.5	0.12	1.32	1.74
74.8°	Benzoyl peroxide	0.066	0.15	0.056	2.87
	<i>p</i> -Chlorobenzoyl peroxide	0.80	0.52	0.042	3.62
61.0°	Benzoyl peroxide	0.0093	0.23	0.0071	4.35
	<i>p</i> -Chlorobenzoyl peroxide	0.012	0.54	0.0055	3.81
49.9°	Benzoyl peroxide	0.0019	0.29	0.0013	5.08
	<i>p</i> -Chlorobenzoyl peroxide	0.003	0.72	0.0008	4.81
34.8°	Benzoyl peroxide	0.00014	0.39	0.00057	6.40
	<i>p</i> -Chlorobenzoyl peroxide	0.00030	0.81	0.000057	5.48

\*In this case the values of  $\mu_{sp}$  are as expected.

This peculiar behaviour of *p*-chlorobenzoyl peroxide may be explained by observing that *w* is always greater in this case than that of benzoyl peroxide. *w* is all the peroxide molecules which do not initiate a polymerization chain and hence must include also the amount used in radical termination process, and this process is more prominent in the former case

than in the latter, and we shall show below that this process tends to make the molecular weight lower.

Some similar observations have also been published by Cooper (*Nature*, 1948, **162**, 897, 927) in two very recent notes.

#### The Size Distribution Function

In the case of termination by combination, Herrington and Robertson give for the size distribution function,

$$\frac{d[M_r]}{dt} = \frac{1}{2} \frac{A^2 \theta^2}{[M]^2} (r-2) e^{-\sqrt{\frac{A \theta}{[M]}} (r-2)} \quad \dots \quad \dots \quad \dots \quad (7)$$

$$\text{where } \theta = \sqrt{\frac{k_t}{k_p}}$$

and  $M$ , the concentration of the polymer with chain length  $r$ .  $A$  is the rate of initiation of the growing chain i.e.,  $A = k_i c = \sum_1^{\infty} k_i [M_i^*]^2$

Equation (7) reduces to

$$\frac{d[M_r]}{dt} = \frac{1}{2} \frac{k_i^2 c^2}{[M]^2} \theta^2 (r-2) e^{-\frac{(r-2) k_i^{\frac{1}{2}} c_i^{\frac{1}{2}} \theta}{M}} \quad \dots \quad \dots \quad \dots \quad \dots \quad (8)$$

This equation is peculiar in the respect that there is a maxima in the  $\frac{d[M_r]}{dt}$  versus  $r$  curve.

As we have mentioned in the beginning that this is the strongest argument in favour of a combination termination in actual polymerization process, as Schulz (*loc. cit.*) pointed out, and his experimental curves have a very close resemblance to equation (8). However, Herrington (*loc. cit.*) points out that a maximum in the size distribution curve may arise from other mechanisms, but all these could at once be eliminated by kinetic considerations.

For the case of termination exclusively by catalyst radical, the molecular distribution can be easily arrived at by a process essentially that of Herrington and Robertson, as shown below. We have,

$$\frac{d[M^*]}{dt} = k_p [M^*_{r-1}][M] - k_p [M^*_r][M] - k_{t2} [M^*_r][R] = 0$$

And if we write  $A$  for the initiation rates of the radical chains

$$A = k_p [M^*][M] + k_{t2} [M^*_1][R]$$

$$\dots \quad \dots \quad \dots \quad \dots \quad \dots$$

$$k_p [M^*_{r-1}][M] - k_p [M^*_r][M] + k_{t2} [M^*_r][R]$$

Summing to infinity

$$A = k_{t2} [R] \sum_1^{\infty} [M_r]$$

$$= \frac{1}{2} k_i c_i$$

Rearranging the above set of equations we get

$$\begin{aligned} A &= k_1 [M_1^*] [M] \left[ 1 + \frac{k_{t_2} [R]}{k_p [M]} \right] \\ &= k_p [M_1^*] [M] \left[ 1 + \frac{k_{t_2} k_1 c}{2 k_p k_1 [M]^2} \right] \quad (\text{by substituting the values of } [R]) \\ &= k_p [M_1^*] [M] \left[ 1 + \frac{\beta c}{[M]^2} \right] \end{aligned}$$

where  $\beta = \frac{k_{t_2} k_1}{2 k_p k_1}$

The  $r$ th equation of this set being

$$k_p [M_{r-1}^*] [M] = k_p [M_r^*] [M] \left[ 1 + \frac{\beta c}{[M]^2} \right]$$

Multiplying both sides up to  $r$ th equation we get,

$$A = k_p [M_r^*] [M] \left[ 1 + \frac{\beta c}{[M]^2} \right]^r$$

Taking logs and using the approximation

$$\log(1+x) = x \text{ for large values of } x,$$

We get

$$\log A = \log k_p [M_r^*] [M] + r \frac{\beta c}{[M]^2}$$

and thus,

$$\begin{aligned} k_p [M_r^*] [M] &= A e^{-r \frac{\beta c}{[M]^2}} \\ &= \frac{1}{2} k_1 c e^{-r \frac{\beta c}{[M]^2}} \end{aligned}$$

Or

$$[M_r^*] = \frac{k_1 c}{2 k_p [M]} e^{-r \frac{\beta c}{[M]^2}} \quad \dots \quad \dots \quad \dots \quad \dots \quad (9)$$

This is our radical distribution equation.

Now, we have,

$$\frac{d[M_r]}{dt} = k_{t_2} [M_r^*] [R] \quad \dots \quad \dots \quad \dots \quad \dots \quad (10)$$

Substituting the value of  $[M_r^*]$  from the radical distribution equation we have,

$$\frac{d[M_r]}{dt} = \frac{k_{t_2} k_1^2 c^2}{4 k_p k_1 [M]^2} e^{-r \frac{\beta c}{[M]^2}}$$

Writing  $\alpha$  for  $\frac{k_{t_2} k_1^2}{4 k_p k_1}$  we get our required size distribution curve

$$\frac{dM_r}{dt} = \frac{\alpha c^2}{[M]^2} e^{-r \frac{\beta c}{[M]}} \quad \dots \quad \dots \quad \dots \quad \dots \quad (11)$$

The size distribution equation (11) is clearly an exponentially decreasing curve with no maximum. The effect of radical termination occurring concurrently with the usual termination by combination would therefore be to shift the maxima towards lower chain length which might be one of the factors responsible for the unexpected lower molecular weight in Redington's results.

### C O N C L U S I O N

The hypothesis that the peroxide radicals can readily terminate a growing chain brings us face to face with the problem of determination of the factors which make a free radical very effective in such processes. This question naturally is bound with the stability of the free radicals and their average life on which very little is known. Some considerations similar to the alternating effect (Walling and Mayo, *J. Poly. Sci.*, 1948, **3**, 895) in copolymerization may also have some bearing on the problem. As more information on various catalysts is becoming increasingly available, it seems that a complete overlooking of this role of the catalyst radical has been too drastic an oversimplification in many cases.

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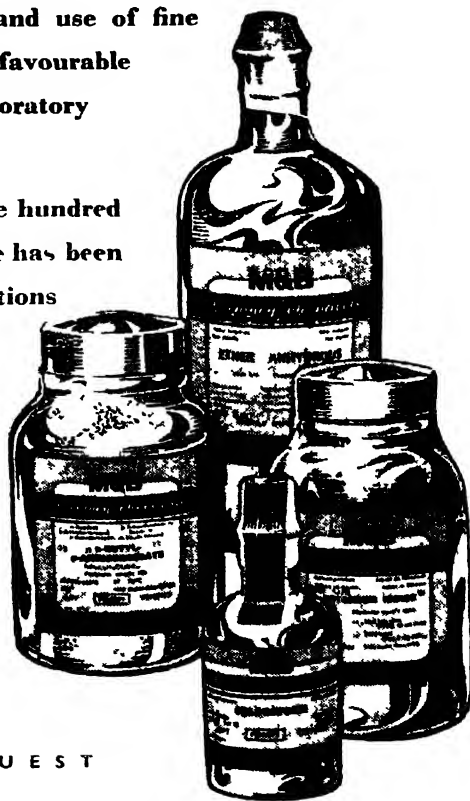
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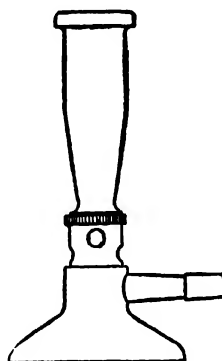
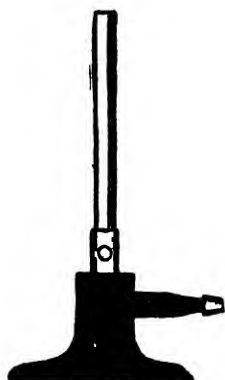
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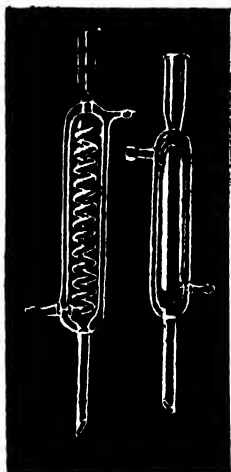
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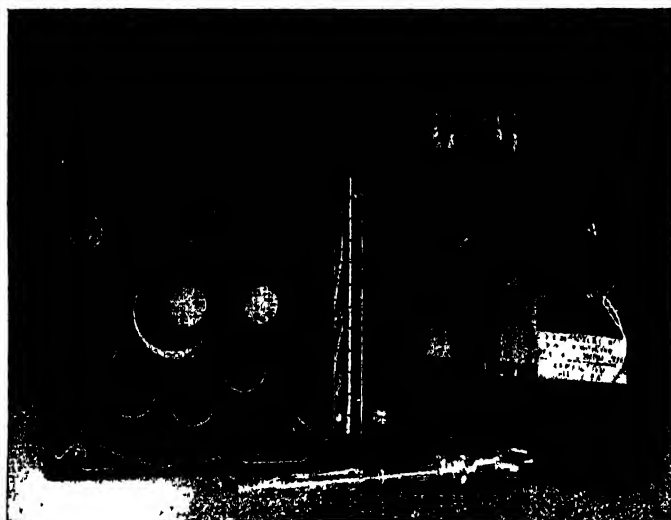
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## CHEMISTRY OF THE RARE EARTHS. PART VI. DOUBLE THIOSULPHATE OF RARE EARTHS

By NIHAR KUMAR DUTT

Composition and isolation of several double thiosulphates of rare earths have been described.

Our knowledge of the thiosulphates of rare earths is very meagre. These have been described in text-books as "well-defined crystalline salts which are readily soluble in water. They are not hydrolysed with the precipitation of basic salts when their aqueous solutions are boiled". The incorrect nature of the above statement was first evident from the observations of Salkar (*Ann. chim.*, 1927, **v**, **8**, 252) who, while working with gadolinium, observed that "gadolinium thiosulphate is not obtained by double decomposition between the calculated quantities of gadolinium sulphate and barium thiosulphate. On evaporation on a water-bath or over conc. sulphuric acid, the product decomposes. A concentrated solution on being precipitated with alcohol gives a compound which is unstable and on keeping becomes insoluble in water with separation of sulphur". Similar observations were made with elements of the cerium group. Their thiosulphates were found to be stable only in dilute aqueous solution and in the presence of a large excess of alkali thiosulphates. Slight decomposition was observed in the yttrium group in concentrated solution by Crookes (*Chem. News*, 1896, **74**, 259). This stability in presence of excess of thiosulphate suggests the formation of double thiosulphate in solution.

Several moderately soluble double thiosulphates of the cerium earths with monovalent copper have been described by Cammeri and Fernandes (*Gazzetts*, 1925, **55**, 443) having the general formula  $\text{RCu}(\text{S}_2\text{O}_4)_2 \cdot 8\text{H}_2\text{O}$ , where R stands for Ce, La, Pr and Nd.

Several bismuthi-thiosulphates of the general formula  $\text{R}_3\text{Bi}(\text{S}_2\text{O}_3)$ , where R stands for Na, K, Rb, Cs,  $\frac{1}{2}$  Ba, have been described by Carnot (*Compt. rend.*, 1876, **83**, 390), Sanchez (*Bull. soc. chim.*, 1912, **iv**, **11**, 440), Hauser (*Z. anorg. Chem.*, 1903, **35**, 1) and Vanino and Muschnug (*Arch. Pharm.*, 1919, **259**, 264). The above observations of Carnot and others and the close resemblances which the rare earth salts show with the corresponding salts of bismuth, at once suggest the existence of double thiosulphate of rare earths. Investigations into their nature and composition form the subject matter of the present communication. Several double thiosulphates have been isolated in the solid stage.

Before proceeding with the actual isolation, we must know their composition and this has been studied by two independent physical methods :

1. Method of thermometric titration of Dutoit (*J. chim. phys.*, 1921, **19** 324, 331).
2. Method of continued variation of Job (*Compt. rend.*, 1928, **180**, 928).

## E X P E R I M E N T A L

*Thermometric titrations : Experimental Arrangements*(cf. Part IV, this *Journal*, 1945, 22, 75).

The solution ( $M/10$ ) of the rare earth nitrate (40 c.c.) was taken in the inner flask and the thiosulphate solution ( $2 M$ ) was added from the burette at regular intervals and the changes in temperatures noted. The differences in temperature were then plotted against the volume in c.c. of the thiosulphate solution added (Figs. 1-4).

The curves for the cerium earths are all of the same type, multilinear with two breaks each, the position of the first break with different rare earths and thiosulphates always lies in the same region where the ratio of  $R : S_2O_3 = 2 : 3$  corresponding to the formation of normal thiosulphate  $R_2(S_2O_3)_3$ , where  $R$  stands for La, Ce, Pr and Nd. So far as the position of the second break in different curves is concerned, however, the curves differ much from one another for different alkali thiosulphate. For sodium thiosulphate (Fig. 1) the second break lies in a region corresponding to the complex ion  $R(S_2O_3)_4^{4-}$ . For K and  $NH_4$ -salts, however (Figs. 2 and 3), the break corresponds to a complex ion  $R(S_2O_3)_3^{3-}$ . Curves for the yttrium salt (Fig. 4), unlike those for the elements of the cerium group, present only one break corresponding to the normal salt  $Y_2(S_2O_3)_3$ . No indication of the formation of any complex salt is obtained.

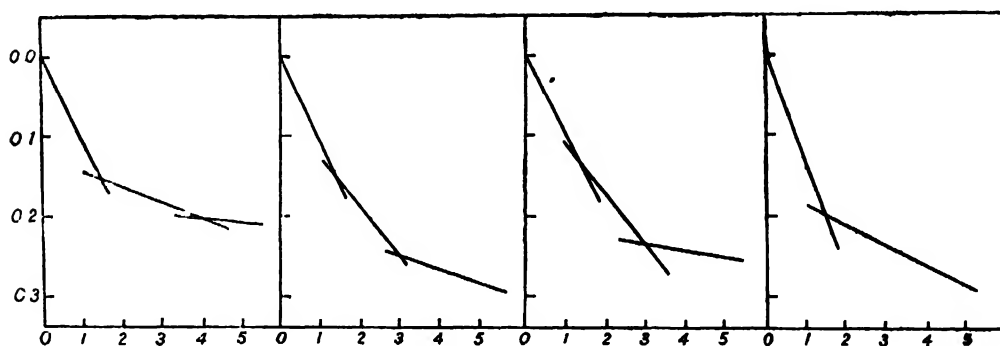
*Thermometric titration curves.*

FIG. 1

FIG. 2

FIG. 3

FIG. 4

*Method of Continued Variation*

This method for the study of imperfect molecular and ionic aggregates in solution and determination of their stabilities is originally due to Job (*loc. cit.*). Suppose the complex thiosulphate is produced by the following equilibrium reaction,



The general equation relating the values of the dissociation constant  $K$ , as derived by Job, is as follows :

$$\frac{C^{m+n-1} \times p^{n-1}}{m^{n-1} \cdot n^{m-1} \cdot (p-1)^{m+n-1}} \times \{(pm+n)x-n\}^{m+n} = K\{n-(m+n)x\} \quad \dots (2)$$

where  $m$  represents mol. of rare earth, R

$n$  „ „ thiosulphate

$C$  „ „ molar conc. of R

$pC$  „ „ thiosulphate.

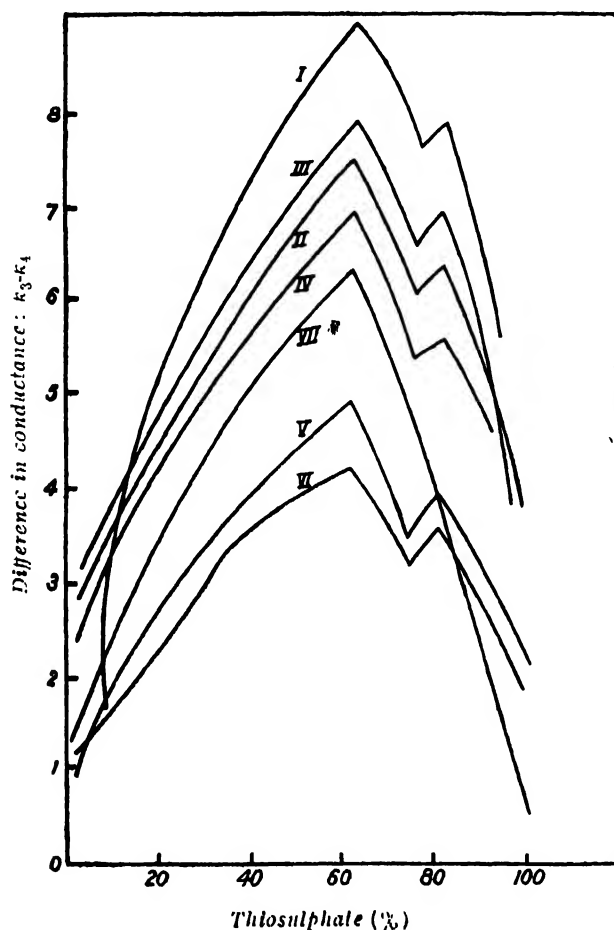
Suppose  $x$  c.c. of thiosulphate combine with  $(1-x)$  c.c. of R to give the maximum change. Putting  $p=1$  in eq. (2), that is for equimolecular solutions, we have

$$\frac{m}{n} = \frac{1-x}{x} \quad \dots (3)$$

Hence from a knowledge of the maximum composition ( $x$ ), the formula of the complex can be determined from the ratio  $m/n$  taking the simplest value for  $m$  and  $n$ .

FIG. 5

Conductometric curves



To determine the maximum composition, changes in conductivities of different solutions were studied. Resistances were actually measured and reciprocals of them were taken as conductivities. The divergencies from additive values (on the assumption that no reaction takes place) were then plotted as a function of the composition of the mixture.

All measurements were made in an electrically regulated thermostat capable of keeping the temperature constant within  $\pm 0.05^\circ$ .

For experimental determination of electrical resistances, much improved and precise method has been employed, which will be discussed in a later communication.

All the curves with different alkali thiosulphate in this case, however, are alike showing breaks in the regions corresponding to the normal thiosulphate and the complex ion  $R(S_2O_3)_4^{4-}$  showing that at these dilutions only one type of complex ion exists in solution, no molecule aggregate as  $R(S_2O_3)_3^{3-}$  exists.

In the solid state, however, two types were isolated.

To prove that the maximum composition is independent of the concentrations of the primary solutions, the above experiments were repeated with solutions of different but equimolecular concentrations, giving identical results. Results for one set of observations are, however, given (Tables I-VII, Fig. 5).

TABLE I

$M/40$ -Lanthanum chloride and  $M/40$ -sodium thiosulphate (Fig. 5, curve 1).

1		2	3		4	5	6		7	8
LaCl <sub>3</sub> .	Water.	$R \times 10^3$ of the soln. in column 1 ( $K_1$ )	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .	Water.	$R \times 10^3$ of the soln. in column 3 ( $K_2$ )	$K_1 + K_2 = K_3$	LaCl <sub>3</sub>	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	$R \times 10^3$ of the soln. in column 7 ( $K_4$ )	For $K_3 - K_4$ .
90 c.c.	10 c.c.	35.012	10 c.c.	90 c.c.	3.077	38.089	90 c.c.	10 c.c.	36.087	2.002
85	15	33.313	15	85	4.632	37.915	85	15	34.240	3.705
80	20	31.464	20	80	5.980	37.144	80	20	32.862	4.582
75	25	29.414	25	75	7.203	36.647	75	25	31.331	5.313
70	30	27.625	30	70	8.602	36.127	70	30	29.975	6.252
65	35	25.616	35	65	9.821	35.437	65	35	28.433	7.004
60	40	24.352	40	60	10.732	35.084	60	40	27.533	7.551
55	45	22.002	45	55	12.303	34.305	55	45	26.301	8.04
50	50	20.832	50	50	13.213	35.045	50	50	25.723	8.322
45	55	18.441	55	45	15.012	33.443	45	55	24.892	8.551
40	60	17.052	60	40	16.321	33.373	40	60	24.621	8.752
35	65	15.253	65	35	18.014	33.267	35	65	24.756	8.511
30	70	13.861	70	30	19.552	33.013	30	70	24.872	8.141
25	75	11.466	75	25	20.812	32.278	25	75	24.955	7.323
20	80	9.725	80	20	22.152	31.877	20	80	24.061	7.816
15	85	7.504	85	15	24.116	31.620	15	85	24.689	6.931
10	90	5.315	90	10	24.502	29.818	10	90	24.186	5.632
5	95	3.971	95	5	26.014	29.928	5	95	25.796	4.132

TABLE II

*M*/50-Lanthanum chloride and *M*/50-pot. thiosulphate (Fig. 5, curve II).

1		2	3		4	5	6		7	8	
LaCl <sub>3</sub>	Water.	$1/R \times 10^3$ of the soln. in column 1 ( $K_1$ ).	$r_2S_2O_3$ .	Water.	$1/R \times 10^3$ of the soln. in column 3 ( $K_2$ ).	$K_1 + K_2 = K_3$ .	LaCl <sub>3</sub> .	$K_2S_2O_3$ .	$1/R \times 10^3$ of the soln. in column 6 ( $K_4$ ).	Diff. ( $K_3 - K_4$ ).	
95	c.c.	5 c.c.	27.313	5 c.c.	95 c.c.	1.616	38.929	95 c.c.	5 c.c.	25.975	2.954
90	10		25.572	10	90	2.713	28.315	90	10	24.930	3.385
85	15		24.202	15	85	1.005	28.207	85	15	24.355	3.852
80	20		23.052	20	80	5.125	28.175	80	20	23.930	1.215
75	25		21.812	25	75	6.112	27.921	75	25	23.171	4.753
70	30		20.592	30	70	6.892	27.184	70	30	22.279	5.05
65	35		19.011	35	65	8.312	27.323	65	35	21.739	5.684
60	40		17.802	40	60	9.382	27.184	60	40	21.182	6.002
55	45		16.331	45	55	10.823	27.151	55	45	20.752	6.402
50	50		14.981	50	50	12.055	27.036	50	50	20.291	6.745
45	55		13.652	55	45	13.086	26.738	45	55	19.751	6.987
40	60		12.424	60	40	14.223	26.647	40	60	19.102	7.245
35	65		11.042	65	35	15.312	26.354	35	65	19.432	6.922
30	70		9.746	70	30	16.204	25.950	30	70	19.462	6.188
25	75		7.952	75	25	17.404	25.356	25	75	19.498	5.858
20	80		6.782	80	20	18.552	25.331	20	80	19.129	6.205
15	85		5.506	85	15	19.802	25.308	15	85	19.706	5.602
10	90		3.954	90	10	21.055	25.009	10	90	20.361	1.648
5	95		2.656	95	5	22.123	24.779	5	95	21.234	3.545

TABLE III

*M*/50-Lanthanum chloride and *M*/50-Am. thiosulphate (Fig. 5, curve III).

1		2	3		4	5	6		7	8	
LaCl <sub>3</sub>	Water	$1/R \times 10^3$ of the soln. in column 1 ( $K_1$ )	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	Water	$1/R \times 10^3$ of the soln. in column 3 ( $K_3$ )	$K_1 + K_2 = K_3$	LaCl <sub>3</sub>	Am <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	$1/R \times 10^3$ of the soln. in column 6 ( $K_4$ )	Diff. $K_3 - K_4$	
95	c.c.	5 c.c.	27.313	5 c.c.	95 c.c.	1.616	38.929	95 c.c.	5 c.c.	26.067	2.862
90	10		25.572	10	90	2.812	28.384	90	10	24.882	3.502
85	15		24.202	15	85	3.952	28.154	85	15	24.069	4.085
80	20		23.052	20	80	5.051	28.123	80	20	23.601	4.502
75	25		21.812	25	75	6.212	28.021	75	25	22.922	5.102
70	30		20.592	30	70	7.311	27.906	70	30	22.301	5.605
65	35		19.011	35	65	8.503	27.514	65	35	21.429	6.085
60	40		17.802	40	60	9.613	27.115	60	40	20.910	6.505
55	45		16.331	45	55	10.803	27.134	55	45	20.229	6.905
50	50		14.981	50	50	12.005	26.936	50	50	19.881	7.105
45	55		13.652	55	45	13.012	26.604	45	55	19.312	7.352
40	60		12.424	60	40	14.113	26.537	40	60	19.035	7.502
35	65		11.042	65	35	15.414	26.456	35	65	19.354	7.102
30	70		9.746	70	30	16.521	26.267	30	70	19.602	6.665
25	75		7.952	75	25	17.812	25.764	25	75	19.809	5.955
20	80		6.782	80	20	18.808	25.590	20	80	19.266	6.324
15	85		5.506	85	15	20.004	25.510	15	85	19.726	5.784
10	90		3.954	90	10	21.253	25.207	10	90	20.152	5.055
5	95		2.656	95	5	22.414	25.070	5	95	20.735	4.335

TABLE IV

M/50-Cerous chloride and M/50-Am. thiosulphate (Fig. 5, curve IV).

1		2	3		4	5	6		7	8	
CeCl <sub>3</sub> .	Water.	$1/R \times 10^3$ of the soln. in column 1 ( $K_1$ ).	Am <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .	Water.	$1/R \times 10^3$ of the soln. in column 3 ( $K_3$ ).	$K_1 + K_2 = K_3$ .	CeCl <sub>3</sub>	Am <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .	$1/R \times 10^3$ of the soln. in column 6 ( $K_4$ ).	Diff. ( $K_3 - K_4$ ).	
95	c.c.	5 c.c.	27.212	5 c.c.	95 c.c.	1.616	38.828	95 c.c.	5 c.c.	25.873	2.955
90	10	25.753	10	90	2.812	28.565	28.565	90	10	24.957	3.615
85	15	24.314	15	85	3.952	28.266	28.266	85	15	24.163	4.103
80	20	23.111	20	80	5.051	28.162	28.162	80	20	23.540	4.622
75	25	21.802	25	75	6.212	28.014	28.014	75	25	22.909	5.115
70	30	20.413	30	70	7.314	27.727	27.727	70	30	22.105	5.622
65	35	19.015	35	65	8.503	27.518	27.518	65	35	21.513	6.005
60	40	17.802	40	60	9.613	27.115	27.115	60	40	20.933	6.482
55	45	16.401	45	55	10.803	27.204	27.204	55	45	20.251	6.953
50	50	15.121	50	50	12.005	27.126	27.126	50	50	19.774	7.352
45	55	13.503	55	45	13.012	26.515	26.515	45	55	18.883	7.632
40	60	12.282	60	40	14.113	26.395	26.395	40	60	18.493	7.902
35	65	10.901	65	35	15.414	26.315	26.315	35	65	18.730	7.585
30	70	9.682	70	30	16.521	26.203	26.203	30	70	19.298	6.905
25	75	8.183	75	25	17.812	25.995	25.995	25	75	19.744	6.251
20	80	6.802	80	20	18.808	25.610	25.610	20	80	19.112	6.498
15	85	5.414	85	15	20.004	25.418	25.418	15	85	19.316	6.102
10	90	4.202	90	10	21.253	25.255	25.255	10	90	19.599	5.656
5	95	2.806	95	5	22.414	25.220	25.220	5	95	20.016	5.204

TABLE V

M/100-Samarium chloride and M/100-sodium thiosulphate (Fig. 5, curve V).

1		2	3		4	5	6		7	8	
SmCl <sub>3</sub> .	Water.	1/R × 10 <sup>3</sup> of the soln. in column 1 (K <sub>1</sub> )	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .	Water.	1/R × 10 <sup>3</sup> of the soln. in column 3 (K <sub>3</sub> ).	K <sub>1</sub> + K <sub>2</sub> = K <sub>3</sub> .	SmCl <sub>3</sub> .	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .	1/R × 10 <sup>3</sup> of the soln. in column 6 (K <sub>4</sub> ).	Diff. K <sub>3</sub> - K <sub>4</sub> .	
95	c.c.	5 c.c.	15.201	5 c.c.	95	1.511	16.712	95 c.c.	5 c.c.	15.874	0.838
90	10	14.412	10	90	2.012	16.124	16.124	90	10	15.199	1.225
85	15	13.651	15	85	2.503	16.254	16.254	85	15	14.569	1.685
80	20	13.212	20	80	3.023	16.236	16.236	80	20	14.131	2.102
75	25	12.402	25	75	3.812	16.212	16.212	75	25	13.558	2.654
70	30	11.732	30	70	4.402	16.134	16.134	70	30	13.046	3.088
65	35	10.801	35	65	5.005	15.806	15.806	65	35	12.321	3.485
60	40	10.313	40	60	5.521	15.834	15.834	60	40	11.939	3.895
55	45	9.203	45	55	6.208	15.411	15.411	55	45	11.266	4.145
50	50	8.414	50	50	6.812	15.226	15.226	50	50	10.831	4.395
45	55	7.903	55	45	7.252	15.155	15.155	45	55	10.540	4.615
40	60	7.002	60	40	8.202	15.204	15.204	40	60	10.309	4.805
35	65	6.314	65	35	8.601	14.915	14.915	35	65	10.470	4.445
30	70	5.611	70	30	9.202	14.813	14.813	30	70	10.811	4.002
25	75	4.812	75	25	9.712	14.524	14.524	25	75	11.049	3.475
20	80	4.011	80	20	10.413	14.424	14.424	20	80	10.622	3.802
15	85	3.013	85	15	11.006	14.019	14.019	15	85	10.734	3.285
10	90	2.153	90	10	11.621	13.774	13.774	10	90	10.989	2.785
5	95	1.414	95	5	12.221	13.635	13.635	5	95	11.703	1.932

TABLE VI

*M*/100-Neodymium chloride and *M*/100-sodium thiosulphate (Fig. 5, curve VI).

1		2	3		4	5	6		7	8
NdCl <sub>3</sub> .	Water.	$1/R \times 10^3$ of the soln. in column 1 ( $K_1$ ).	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .	Water.	$1/R \times 10^3$ of the soln. in column 3 ( $K_3$ ).	$K_1 + K_2 = K_3$ .	NdCl <sub>3</sub> .	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .	$1/R \times 10^3$ of the soln. in column 6 ( $K_4$ ).	Diff. ( $K_3 - K_4$ ).
95 c.c.	5 c.c.	16.423	5 c.c.	95 c.c.	1.743	18.166	95 c.c.	5 c.c.	17.065	1.101
90	10	15.402	10	90	2.029	17.431	90	10	15.846	1.585
85	15	14.352	15	85	2.341	16.693	85	15	14.638	2.005
80	20	13.279	20	80	2.742	16.021	80	20	13.626	2.395
75	25	12.512	25	75	3.455	15.967	75	25	13.212	2.755
70	30	11.828	30	70	4.083	13.911	70	30	12.816	3.095
65	35	11.066	35	65	4.702	15.768	65	35	12.413	3.355
60	40	10.269	40	60	5.298	15.567	60	40	11.980	3.587
55	45	9.362	45	55	5.901	15.263	55	45	11.541	3.722
50	50	8.661	50	50	6.598	15.259	50	50	11.447	3.812
45	55	7.842	55	45	7.101	14.943	45	55	11.038	3.905
40	60	7.121	60	40	7.802	14.923	40	60	10.921	4.002
35	65	6.302	65	35	8.598	11.900	35	65	11.105	3.795
30	70	5.402	70	30	9.042	11.444	30	70	11.209	3.235
25	75	4.532	75	25	9.464	13.996	25	75	11.445	2.551
20	80	3.711	80	20	10.248	13.989	20	80	10.733	3.256
15	85	2.942	85	15	10.816	13.758	15	85	11.083	3.675
10	90	2.021	90	10	11.502	13.523	10	90	11.298	2.225
5	95	1.102	95	5	12.305	13.407	5	95	12.219	1.188

TABLE VII

*M*/50-Yttrium chloride and *M*/50-sodium thiosulphate (Fig. 5, curve VII).

1		2	3		4	5	6		7	8
YtCl <sub>3</sub> .	Water.	$1/R \times 10^3$ of the soln. in column 1 ( $K_1$ ).	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .	Water.	$1/R \times 10^3$ of the soln. in column 3 ( $K_3$ ).	$K_1 + K_2 = K_3$ .	YtCl <sub>3</sub> .	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .	$1/R \times 10^3$ of the soln. in column 6 ( $K_4$ ).	Diff. ( $K_3 - K_4$ ).
95 c.c.	5 c.c.	26.412 c.c.	5 c.c.	95 c.c.	1.202	27.614	95 c.c.	5 c.c.	26.109	1.505
90	10	25.103	10	90	2.651	27.754	90	10	25.659	2.095
85	15	23.851	15	85	3.611	27.462	85	15	24.680	2.782
80	20	22.313	20	80	5.024	27.345	80	20	24.153	3.192
75	25	21.302	25	75	6.024	27.326	75	25	23.601	3.725
70	30	20.121	30	70	6.911	27.062	70	30	23.007	4.055
65	35	18.513	35	65	8.302	26.815	65	35	22.261	4.554
60	40	17.402	40	60	9.302	26.794	60	40	21.909	4.885
55	45	16.001	45	55	10.514	26.515	55	45	21.410	5.105
50	50	14.491	50	50	11.735	26.227	50	50	20.842	5.385
45	55	13.122	55	45	12.616	25.738	45	55	20.183	5.555
40	60	12.092	60	40	13.524	25.606	40	60	19.904	5.702
35	65	10.501	65	35	15.012	25.513	35	65	20.118	5.395
30	70	9.441	70	30	15.823	25.264	30	70	20.346	4.918
25	75	7.736	75	25	17.314	25.050	25	75	20.595	4.455
20	80	6.672	80	20	18.256	24.928	20	80	21.016	3.912
15	85	5.124	85	15	19.482	24.006	15	85	21.701	2.905
10	90	3.474	90	10	20.451	23.925	10	90	21.723	2.202
5	95	2.302	95	5	21.616	23.918	5	95	22.616	1.302

*Preparation of the Complex Thiosulphates in the Solid State*

After determining the composition of the complex by the physical methods, the investigation was extended to the isolation of these salts in the solid state.

1. *Sodium Lanthanum Thiosulphate*.—For the preparation of the sodium salts, rare earths were taken as perchlorates, since sodium perchlorate that would be formed by double decomposition is soluble in alcohol.

Lanthanum perchlorate (1 g.) was taken in 5 c.c. of water, cooled in ice to  $0-2^{\circ}$ ; to this solution was then added a well cooled solution of sodium thiosulphate (2 g.) in 5 c.c. of water with stirring. Alcohol (50 c.c., 95%), cooled in ice, was then added dropwise and stirred mechanically; at first an oil separated which was quickly transformed into white crystalline precipitate. It was then purified by washing with 95% alcohol first by decantation and then on the filter. It was then redissolved in the least quantity of ice-water and reprecipitated with alcohol, washed similarly as above, and dried in a vacuum desiccator over  $\text{CaCl}_2$ .

The salts separate in colorless micro-crystals, readily soluble in water. An aqueous solution decomposes gradually becoming turbid due to the separation of sulphur. [Found: Na, 16.51; La, 19.81; S, 36.05.  $\text{Na}_3\text{La}(\text{S}_2\text{O}_3)_3$  requires Na, 16.41; La, 19.82; S, 36.41 per cent].

2. *Sodium Cerium Thiosulphate*.—The method of preparation is the same as above using cerous perchlorate. In properties the salt resembles the lanthanum salt in all respects. [Found: Na, 16.50; Ce, 20.11; S, 36.31.  $\text{Na}_3\text{Ce}(\text{S}_2\text{O}_3)_3$  requires Na, 16.35; Ce, 19.91; S, 36.41 per cent].

3. *Sodium Praseodymium Thiosulphate*.—Praseodymium perchlorate (1 g.) was taken in 5 c.c. of ice-cold water. The rest of the procedure was the same as above. The salt separated in light green micro-crystals. In other respects it resembles the other salts. [Found: Na, 16.21; Pr, 20.14; S, 36.52.  $\text{Na}_3\text{Pr}(\text{S}_2\text{O}_3)_3$  requires Na, 16.33; Pr, 20.01; S, 36.33 per cent].

4. *Sodium Neodymium Thiosulphate*.—The method of preparation is the same as above using neodymium perchlorate. The salt has a light rose colour. [Found: Na, 16.14; Nd, 20.44; S, 36.33.  $\text{Na}_3\text{Nd}(\text{S}_2\text{O}_3)_3$  requires Na, 16.26; Nd, 20.40; S, 36.18 per cent].

5. *Potassium Lanthanum Thiosulphate*.—For the preparation of potassium salts, rare earth acetates were taken to start with, since potassium acetate is highly soluble in alcohol.

Lanthanum acetate (1 g.) was taken in 5 c.c. of ice-cold water; to this solution was then added a well-cooled solution of potassium thiosulphate (1.6 g.) in 5 c.c. of water with stirring; alcohol (50-60 c.c., 95%) cooled in ice was then added drop by drop with mechanical stirring, when at first an oil separated which was quickly transformed into a microcrystalline precipitate. It was washed with 95% alcohol, filtered, redissolved in the least quantity of ice-water and reprecipitated with alcohol, washed as above, filtered and dried in a vacuum desiccator over  $\text{CaCl}_2$ .



The salt separates in white micro-crystalline state. In composition, it resembles the corresponding salt of bismuth, unlike which, however, it is readily soluble in water with gradual decomposition with separation of S. [Found : K, 19.58 ; La, 23.32 ; S, 32.71.  $K_3La(S_2O_3)_3$  requires K, 19.76 ; La, 23.48 ; S, 32.43 per cent].

6. *Potassium Cerium Thiosulphate*.—The method of preparation is the same as above substituting cerous acetate in place of lanthanum acetate. It resembles the lanthanum salt in all respects. [Found : K, 19.57 ; Ce, 23.65 ; S, 32.60.  $K_3Ce(S_2O_3)_3$  requires K, 19.73 ; Ce, 23.61 ; S 32.37 per cent].

7. *Potassium Praseodymium Thiosulphate*.—The salt was prepared in the same way as the other salts from praseodymium acetate and potassium thiosulphate. The salt separates in light green micro-crystals, readily soluble in water with decomposition. [Found : K, 19.57 ; Pr, 23.72 ; S 32.45.  $K_3Pr(S_2O_3)_3$  requires K, 19.69 ; Pr, 23.73, S, 32.32 per cent].

8. *Potassium Neodymium Thiosulphate*.—The method of preparation is the same as above which it resembles in all respects. The salt is obtained in light rose colour. [Found : K, 19.65 ; Nd, 24.06 ; S, 32.31.  $K_3Nd(S_2O_3)_3$  requires K, 19.59 ; Nd, 24.16 ; S, 32.14 per cent].

9. *Ammonium Lanthanum Thiosulphate*.—For the preparation of the ammonium salts the rare earth iodides are used. The salt is obtained from lanthanum iodide and ammonium thiosulphate in the same way as other alkali salts.

The ammonium salts, also, have the composition similar to the corresponding bismuth salts. It is readily soluble in water and the aqueous solution decomposes gradually with separation of sulphur. [Found :  $NH_4$ , 10.12 ; La, 26.15 ; S, 36.36.  $(NH_4)_3La(S_2O_3)_3$  requires  $NH_4$ , 10.21 ; La, 26.28 ; S 36.20 per cent].

10. *Ammonium cerium thiosulphate* was prepared in same way as above. [Found :  $NH_4$ , 10.16 ; Ce, 26.38 ; S, 36.14.  $(NH_4)_3Ce(S_2O_3)_3$  requires  $NH_4$ , 10.19 ; Ce, 26.47 ; S, 36.23 per cent].

11. *Ammonium Praseodymium Thiosulphate*.—The method of preparation is the same as above. The salt separates in green micro-crystalline precipitate. [Found :  $NH_4$ , 10.12 ; Pr, 26.48 ; S, 36.24.  $(NH_4)_3Pr(S_2O_3)_3$  requires  $NH_4$ , 10.17 ; Pr, 26.55 ; S, 36.16 per cent].

12. *Ammonium neodymium thiosulphate* was obtained as above as light rose crystals. It readily dissolves in water with gradual decomposition with separation of sulphur. [Found :  $NH_4$ , 10.21 ; Nd, 27.12 ; S, 36.15.  $(NH_4)_3Nd(S_2O_3)_3$  requires  $NH_4$ , 10.11 ; Nd, 27.02 ; S, 35.96 per cent].

#### Methods of Analysis

The compound was first decomposed with concentrated hydrochloric acid and filtered. The rare earths were precipitated from this filtrate twice with ammonia, the hydroxides

dissolved in dilute hydrochloric acid and precipitated with oxalic acid as oxalates and the oxalates were then ignited to oxides. The filtrates from ammonia precipitation were mixed together, evaporated to dryness, ammonium salts removed by ignition, residue treated with a few drops of concentrated sulphuric acid, excess removed and alkalis weighed as sulphate. Sulphur was estimated in a separate sample as  $\text{BaSO}_4$  after oxidation with ammoniacal hydrogen peroxide and separation of rare earth hydroxides. Ammonium in ammonium salts were estimated by Kjeldahl's method after distillation with caustic soda, absorbing the evolved ammonia in standard acid and titrating the excess acid back with standard alkali.

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## CHROMATOGRAPHIC ESTIMATION OF ALLOYS. PART I. COPPER IN BRASS AND BRONZE

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Conditions for obtaining uniform and sharp chromatograms of copper ion has been studied with reference to the adsorbent, size of tube, strength of solution and developer. Using potassium ferrocyanide as developer, a method of estimating copper by the use of adsorption isotherm has been evolved. The method has been used to estimate copper in brass and bronze to an accuracy of 99%.

Lange and Nadel (*Z. Elektrochem.*, 1936, **42**, 210) and Schwab and co-workers (*Naturwiss.*, 1937, **28**, 44 ; *Z. angew. Chem.*, 1937, **50**, 546, 691; 1938, **51**, 709) have made considerable contribution to the study of inorganic chromatography and laid down conditions under which chromatograms could be obtained. However, less attention has been paid till now to inorganic than to organic aspect of the subject on the quantitative side. Cook (Lecture on chromatographic analysis, Institute of Chemistry of Great Britain and Ireland, 1941, p. 29) draws attention to the promising field of chromatographic estimation of one ion from the dimensions of the chromatic zone and the value of this method in the analysis of steel and other alloys. Since this method is elegant and should prove useful in the rapid analysis of a large number of alloys in any technical laboratory, investigations on the quantitative analysis of brass and bronze were undertaken by this. It could be seen from the experimental details, mentioned below, that great care has to be taken to get absolutely sharp bands and uniform zones.

### EXPERIMENTAL

*Preparation of the Adsorbent*—Alumina used in this investigation was prepared as follows: Pure potash alum (500 g.) was dissolved in water to make a saturated solution and strong ammonia added in small quantities, while the solution was kept stirred and warm. The precipitated alumina was taken up with a large quantity of distilled water, decanted and filtered. The precipitate was washed several times with distilled water to remove the last traces of sulphates and ammonia, and dried at 120°. The dry alumina was powdered and sieved at 100 to 120 mesh; this sample was used as the adsorbent.

*Arrangement of the Column*.—The apparatus used was the simple one, similar to the one described by Teswett (*Ber. Deut. bot. Ges.*, 1906, **24**, 384) with or without suction. Schwab and co-workers (*loc. cit.*) filled the tube with a thick suspension of alumina and heated it to 70° to 80° to make it air-free and to obtain a workable packing by alternate sharp suction and tapping. Trials likewise here proved not satisfactory to get sharp and well defined separation. The end of the chromatogram was not sharp but showed a saw-edged appearance. Further, on allowing the column to drain itself after washing with water it was found that small air bubbles still remained which, while working, slowly moved with the liquid passing through and produced diffuse extension of the chromatogram at the walls of the tube.

It has also been mentioned by the above workers that alumina shows good adsorption if moistened with a liquid of  $p_H$  value of 9.4. In view of these the following procedure was adopted and was found to give sharp bands without any diffusion.

Tubes (25 cm. long and proper width, as described and decided by the following

experiments) were filled with the prepared alumina made into a paste with water  $p_n$  of which was adjusted to 9.4 by the addition of a small quantity of ammonia. The  $p_n$  was noted by the addition of B.D.H. Universal indicator so that a portion of the water gave greenish blue colour with green predominating. The tubes so filled were immersed in a tall jar of water of the same  $p_n$  and kept overnight. It was found by this procedure that all the air-bubbles were slowly removed and there was complete elimination of non-uniform packing. The results were remarkably good in that there was absolutely no diffusion or saw-edged end of the band. The tubes at the lower ends at the constriction contained a small piece of asbestos wool plug.

*The Choice of the Diameter and the Quantity of Solution to be Tested.*—The prepared column was set up over a filter flask and a gentle suction applied. It was washed several times with water taking care that the top of the column there was always in water or solution and no air was sucked through the column. Measured amounts of  $M/200$  solution of copper nitrate were added gently by pouring it at the top. Gentle suction was applied; it was washed five times with water. The chromatogram was developed by 2 c. c. of ammonium sulphide solution saturated with  $H_2S$ . A few preliminary trials showed that copper nitrate 1 to 5 c. c. solution of strength  $M/200$  and tubes of 0.7 cm. diameter gave suitable lengths of bands, which were sharp and uniform. The results could be reproduced.

*The Choice of the Developer.*—A solution of ammonium sulphide, saturated with hydrogen sulphide, was usually used by Schwab and others for chromatographing copper. The band is black in colour. For zinc the colour is yellow with the adsorption of ammonium sulphide. Experiments were also tried with potassium ferrocyanide as the developer; copper gives the usual brown-red colour and zinc has no colour. The following table gives the observations on the development of the chromatogram of copper with these developers at different concentrations of the solutions of copper.

TABLE I

Adsorbent: alumina, pure B.D.H. from stock.

Quantity of the solution = 1 c.c. of copper nitrate.

Conc. of the soln.	Length of band.	Remarks.
(NH <sub>4</sub> ) <sub>2</sub> S saturated with H <sub>2</sub> S as developer.		
$M/25$	7.0 cm.	Uniform with a little diffusion at the end
$M/50$	3.7	Uniform and better than previous one
$M/100$	1.8	Good and sharp band
$M/200$	0.9	Good and very sharp band
Potassium ferrocyanide as developer.		
$M/25$	7.0 cm.	Good but not uniform
$M/50$	3.6	The band better than with ammonium sulphide
$M/100$	1.7	Sharp band, good and no diffusion
$M/200$	0.85	Beautiful brown band with a sharp line of demarcation between the white and the brown zones

At lower concentration of the solution the adsorption was good.

Next experiments were conducted by converting the copper solution into its complex with ammonia. The following table gives the data.

TABLE II

The conditions are the same as in Table I.  
Cuprammonium complex.

Conc.	Length of band.	Remarks
M/50	8.0 cm.	
M/100	6.1	Pale blue band, uniform and very sharp. No diffusion in all cases
M/200	4.6	
M/400	3.4	
M/800	2.4	

Having now obtained the conditions for obtaining the best chromatogram for the copper ion, the quantitative estimation of copper in the alloys was undertaken. The adsorbent used in the estimation was the one prepared as described in the beginning of this paper.

*Estimation of Copper from the Dimensions of the Chromatograms.*—Martin and Synge (*Biochem. J.*, 1941, **35**, 1358) in their studies on partition chromatography have compared the adsorption column to the fractional distillation column and have derived expressions for known concentrations of the substance adsorbed at every stage of the chromatogram. But in these cases of inorganic salts, the adsorption of the metallic ion is strong and irreversible. The chromatograms could be made to be uniform throughout by carefully adjusting the conditions and working with dilute solutions. In dilute solution as the liquid descends, the cations are completely adsorbed at each layer and the band is uniform. Thus the process is not one of equilibrium at each stage. There is also absence of information in the case of adsorption chromatograms about the effect of concentration on the adsorption coefficient, even if there be equilibrium. Hence, the safest guide available in all adsorption processes is the Freundlich's equation and it could be used to find a relation between the length of the adsorbed column and the quantity of the metal ion (here copper).

Thus,

$$x/m = a C^{1/n}$$

where the symbols have the usual significance.

Under uniform adsorption from dilute solutions,

$$x/m = v/\pi r^2 \cdot h \cdot d$$

where  $r$  is the radius of the tube and  $h$  is the height of the chromatogram and  $d$ , the density of the adsorbent.

For different concentrations  $C_1$  and  $C_2$ ,

$$(C_1/C_2)^{1/n} = h_2/h_1$$

where  $h_1$  and  $h_2$  correspond to the length of the chromatogram at  $C_1$  and  $C_2$  respectively. For different values of  $C$  and  $h$  one can obtain values of  $n$  for each ion measured chromatographically with suitable dimensioned tubes.

Thus, for copper with the alumina, prepared as mentioned above, with a tube of diameter of 0.7 cm. we get using 2 c. c. of the solution and developing with potassium ferrocyanide the following height of chromatograms.

TABLE III

Conc.	Height of chromatogram.	$1/n$ .
(a) $M/25$	1.50 cm.	-1.23 between (d) and (a)
(b) $M/50$	1.95	-1.23 „ (b) and (c)
(c) $M/100$	0.85	-1.23 „ (b) and (a)
(d) $M/200$	0.35	-1.44 „ (c) and (d)

The constancy of the factor  $1/n$  between different concentrations of copper nitrate solutions shows that the above equation could be applied to estimate metallic ions in solution.

The equation applied to data presented in Table II with cuprammonium complex gives a constant of -0.38.

The above quantitative method developed has been applied to the estimation of copper in brass and bronze and the results compared with that obtained by iodimetric estimation of copper in the same samples.

*Estimation of Copper in Brass and Bronze.*—Weighed quantities of less than a gram of the alloys were dissolved in concentrated nitric acid and the solution was made up to 200 c. c. The above solution (2 c. c.) was allowed to pass through the adsorbent. The column was washed with distilled water five times. The alumina used in these experiments was the one prepared from alum as described previously.

The developer used was potassium ferrocyanide. The ammonium sulphide developer was not used since there was a tendency for slight diffusion at the Cu—Zn interface. A number of chromatograms was prepared. The length of the column in each was the same. The alloys used were standard ones supplied by Flatters and Garnett, Manchester, with certificate of analysis. The results are tabulated below.

TABLE IV

*Copper in brass and bronze*Factor  $1/n = -1.23$ .

Wt. of material.	Height of column.	Cu analysed iodimetrically.	Cu values given by Suppliers.	Cu estimated chromatographically.
Brass 1				
0.6580 g	5.50 cm	90.25%	90.00%	90.67%
0.9670	4.20	50.01	50.00	49.56
Bronze 2				
0.7162	4.50	70.15	70.00	70.70

The accuracy of 99%, as obtained above by this method, is fairly good for rapid analysis of a number of samples. For different cations the value of  $1/n$  under conditions of experiment has to be found out and used.

## STUDIES ON VITAMIN-A IN SOLUTION. PART I. STABILITY

BY U. P. BASU AND SUKHAMOY BHATTACHARYA

Stability of vitamin-A in different diluents has been studied both with and without the addition of antioxidants. Unsaturation in diluent is not the sole cause of deterioration of vitamin-A molecule in solution. The antioxidant is found to exert a better effect in protecting the vitamin-A molecule when the system contains an ester (saturated or unsaturated) or a glyceride. In such case no difference has been noticed between the two antioxidants, methylhydroquinone or propyl gallate. Details of vitamin-A assay have also been described.

From economic and commercial points of view the preparation of vitamin-A in suitable vegetable oil is now being advocated. The oil may, however, develop rancidity due to the formation of peroxides, and these peroxides would destroy the vitamin potency. This oxidation may be controlled to a considerable extent by the incorporation of some suitable antioxidant (Whipple, *Oil & Soap*, 1936, **13**, 231; Lowen *et al.*, *Ind. Eng. Chem.*, 1937, **29**, 151; Basu, *Ann. Biochem. Exp. Med.*, 1941, **1**, 165). The nature of the solvent would considerably play a role on the stability of the vitamin (cf. Basu, *loc. cit.*). Sesame oil has been found by Sen Gupta (this *Journal*, 1946, **23**, 233) to destroy the vitamin-A potency of shark liver oil (cf. also Basu and Ray, *Science & Culture*, 1947, **13**, 73). The stability of vitamin-A in different solvents and that again in presence of different antioxidants in varying concentrations have been studied and described in the present paper. The mode of oxidation has been discussed in Part II of this paper.

The vitamin-A in the preparation was estimated by means of an Adam-Hilger's vitameter-A in the oil or ester solution after saponification, when the concentration was low (below 10,000 I.U. per g.) and when present in concentrated form or in liquid paraffin, directly by dissolving in alcohol or in a mixture of ether and alcohol respectively. Details of the methods of estimation are recorded in the experimental part.

### EXPERIMENTAL

**Materials.**—The vitamin used was a vitamin A concentrate made by saponification containing 0.2 million I.U. per g.

The refined and deodorised arachis oil, as obtained from the market, was further dried by shaking with freshly heated and cooled anhydrous sodium sulphate and kept in a glass stoppered bottle overnight, and filtered under suction through a dry Buchner. Liquid paraffin of B. P. specification was similarly dried and purified. Ethyl oleate and ethyl stearate were prepared in the laboratory and the fractions distilling between 196° and 206° under 7-8 mm. pressure in each case were collected and stored in glass stoppered bottles. Glyceryl monolaurate was purchased from the market (Glyco Products Co. U.S.A.). The specification and the characteristic of the diluents are shown in Table I.

TABLE I

*Characteristics of solvents.*

Characteristics.	Arachis oil.	Ethyl oleate.	Ethyl stearate.	Glyceryl monolaurate & liquid paraffin (1:1).
Acid value	Nil	Nil	0.08	5.02
Sap. value	185	—	180.0	105.0
Iodine value	92.8	80.7	1.05	4.0
Rancidity (U. S. P. xiii)	Nil	—	—	—
Unsaponifiable matter	0.48%	Nil	—	—
Refractive index	1.4634/40°	1.4497/25°	—	1.4699/25°
Specific gravity	0.9144/25°	0.8682/25°	—	0.9326/25°
Peroxide value	—	Passes B.P. test	Nil	Nil

The antioxidants used were methylhydroquinone (m.p. 54-56°) and *n*-propyl gallate (m.p. 146-48°) prepared in the laboratory. The concentrations used were 0.02% and 0.05% in the former case and 0.02, 0.05 and 0.1% in the latter.

*Aeration.*—The vitamin-A concentrate was carefully weighed into a special container and suitably diluted with different solvents. The different solutions were then transferred to amber colored resistant glass bottles fitted with perforated corks that allowed introduction of glass tubings for aeration. Antioxidants were directly weighed into the aeration bottles; in case of liquid paraffin, propyl gallate had to be dissolved by addition of a few drops of peroxide-free ether. Usually 25 c.c. of the solutions were used for each experiment. The whole was set up in diffused light and air, purified and dried by passing through sulphuric acid and soda lime tower, was passed (4 c.c. per second) through the systems kept at the room temperature (28°-29°) in all cases except the preparation made with glyceryl monolaurate *cum* liquid paraffin (1:1) where the system was kept in a thermostat adjusted to 33° in order to maintain the preparation in the liquid state.

*Estimation of Vitamin-A.*—Before aeration the vitamin potency was estimated in each case, and then during aeration samples were taken out from the system at intervals for determination of vitamin-A. The whole procedure is described below.

*Apparatus and Reagents.*—Care was taken that the appliances used were absolutely free from any metallic or other impurities and were specially reserved for this purpose. The stop-cocks of the separating funnel were not lubricated with ordinary grease or any ether-soluble lubricant. A starch-glycerin lubricant, as described by Herrington and Starr (*Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 62) was found suitable.

The sample (2g approx.) was saponified for 15-20 minutes. The unsaponifiable matter was extracted in the usual way with peroxide-free ether and the ether extract was dried in nitrogen atmosphere. The dried extract was immediately taken up in aldehyde-free alcohol (12 c.c.) in case of pure oil or ester and peroxide-free, dried ether (12 c.c.) in case where it was mixed up with liquid paraffin. The volume was made up to 25 c.c. in each case with absolute and aldehyde-free alcohol. In most cases this solution had to be diluted further to have the vitameter A reading within the range of 6 to 9.

In case of pure liquid paraffin system, 0.2 to 0.5 g. of the sample was directly weighed



into a 25 c.c. volumetric flask, dissolved in ether and alcohol (1:1) mixture, diluted if necessary and the vitameter A reading was taken as usual.

The potency of the vitamin-A (I.U. per g.) as recorded in various tables below was found out from the formula  $X \times 1600/Y$ , where  $X$  = vitameter A reading and  $Y$  = percentage strength of the sample taken in the vitameter cell.

Liquid paraffin being insoluble in alcohol, the samples from this system were taken in ether-alcohol mixture and in order to find out that this change of solvent would not affect the vitameter A reading, control experiments were carried out with (1) pure alcohol, (2) pure ether, (3) mixture of alcohol and ether (1:1) and (4) a solution containing 0.2 g. of liquid paraffin per 25 c.c. of a similar mixture of alcohol and ether. From the result in Table X it would be evident that the above change in the nature of the solvent did not affect the vitameter reading.

TABLE II

*Arachis oil.*

Aerated for.	Without antioxidant		With 0.05% propyl gallate	
	Vitamin-A (I. U./g.).	% Loss of vitamin-A.	Vitamin-A (I. U./g.).	% Loss of vitamin-A.
0	728	0	728	0
52 hrs.	300	58.8	—	—
66	—	—	574	21.1
100	195	73.2	—	—
128	—	—	534	26.6
149	173	76.2	—	—
177	—	—	500	31.3

TABLE III

*Ethyl oleate.*

Aerated for.	Without antioxidant		With 0.05% propyl gallate	
	Vitamin-A (I. U./g.).	% Loss of vitamin-A.	Vitamin-A (I. U./g.).	% Loss of vitamin-A.
0	740	0	740	0
52 hrs.	300	59.5	—	—
66	—	—	591	20.1
94	196	73.5	—	—
100	—	—	530	28.4
149	190	74.3	—	—
160	—	—	510	31.1

TABLE IV

*Ethyl stearate.*

Aerated for.	Without antioxidant		With 0.05% propyl gallate	
	Vitamin-A (I. U./g.).	% Loss of Vitamin-A.	Vitamin-A (I. U./g.).	% Loss of vitamin-A.
0	700	0	700	0
59 hrs.	480	31.4	—	—
73	—	—	661	5.6
100	408	41.7	—	—
135	—	—	555	20.7
156	372	46.9	—	—
184	—	—	182	31.1

TABLE V

*Liquid paraffin.*

Aerated for.	Without antioxidant		With 0.05% propyl gallate	
	Vitamin-A (I. U./g.).	% Loss of Vitamin-A.	Vitamin-A (I. U./g.).	% Loss of vitamin-A
0	1100	0	1100	0
87 hrs.	512	53.5	658	40.2
142	305	72.3	620	43.7
191	222	79.8	610	44.6

TABLE VI

*Liquid paraffin cum ethyl oleate (1 : 1).*

Aerated for.	Without antioxidant		With 0.05% propyl gallate	
	Vitamin-A (I. U./g.).	% Loss of vitamin-A.	Vitamin-A (I. U./g.).	% Loss of vitamin-A.
0	700	0	700	0
70 hrs.	203	71	—	—
77	—	—	568	18.9
155	150	78.6	—	—
162	—	—	475	32.1
197	125	82.1	450	35.7

TABLE VII

*Liquid paraffin cum ethyl stearate (1 : 1).*

Aerated for.	Without antioxidant		With 0.05% propyl gallate	
	Vitamin-A (I. U./g.).	% Loss of vitamin-A.	Vitamin-A (I. U./g.).	% Loss of vitamin-A.
0	650	0	650	0
42 hrs.	600	7.7	—	—
63	—	—	627	3.5
141	349	46.3	—	—
148	—	—	545	16.2
177	254	62.9	—	—
185	—	—	489	24.8

TABLE VIII

*Liquid paraffin cum glyceryl monolaurate (1 : 1).*

Aerated for.	Without antioxidant		With 0.05% Propyl gallate	
	Vitamin-A (I. U./g.).	% Loss of vitamin-A.	Vitamin-A (I. U./g.).	% Loss of vitamin-A.
0	750	0	750	0
59 hrs.	584	22.1	—	—
66	—	—	712	5.1
100	360	52.0	—	—
108	—	—	672	10.4
170	235	68.7	—	—
177	—	—	648	13.6
230	213	71.6	—	—
238	—	—	617	17.7

TABLE IX

*Arachis oil : Variation of proportions and nature of antioxidant.*

Aerated for.	0.02% Monomethyl hydroquinone.		0.05% Monomethyl hydroquinone.		0.02% Propyl gallate		0.05% Propyl gallate.		0.1% Propyl gallate	
	Vitamin-A (I. U./g.).	% Loss of vitamin-A.	Vitamin-A (I. U./g.).	% Loss of vitamin-A.	Vitamin-A (I. U./g.).	% Loss of vitamin-A.	Vitamin-A (I. U./g.).	% Loss of vitamin-A.	Vitamin-A (I. U./g.).	% Loss of vitamin-A.
0	900	0	900	0	900	0	900	0	900	0
42 hrs.	760	15.6	751	16.2	732	18.7	780	13.3	765	15.0
90	520	42.2	512	43.1	503	44.1	515	42.8	525	41.7
150	468	48.0	475	47.3	472	47.6	485	46.1	490	45.6

TABLE X

*Effect of solvent in vitameter reading.*

No.	Description	Vitameter reading
1	Cell with pure alcohol	0.1
2	„ „ „ ether	0.1
3	„ „ alcohol-ether (1 : 1)	0.1
4	„ „ „ containing 0.2 g. liquid paraffin	0.1

## DISCUSSION

From the Tables II and III it would be noticed that the rate of loss of potency of vitamin-A on aeration, both in presence and in absence of antioxidant, is almost the same in case of a natural glyceride (arachis oil) or an artificial ester made from an unsaturated acid (ethyl oleate). In case of an ester from a saturated fatty acid (ethyl stearate), the loss in absence of an antioxidant is somewhat less (Table IV) showing thereby that the unsaturation of the diluent plays a part in the deterioration of vitamin-A in absence of antioxidant. When the antioxidant is present, the rate is, however, comparable to those of the former two cases. From the data in Table V it appears that the above loss in potency is not due to the onset of oxidation in the fat molecule alone, since in the case of liquid paraffin, a saturated system, the vitamin undergoes more deterioration. That an ester molecule in presence of an antioxidant seems to play a role in inhibiting the oxidation is again evident from the results of experiments as carried out with the systems liquid paraffin containing ethyl stearate (Table VII), glyceryl monolaurate (Table VIII) and ethyl oleate (Table VI). From Table V, it may be noticed that the antioxidant also inhibits the oxidation of the vitamin molecule even when present in liquid paraffin system (cf. Basu and Bhattacharya, *Science & Culture*, 1949, **14**, 481).

The observations, as recorded in Table IX, indicate that in the systems studied methylhydroquinone behaves in the same way as propyl gallate and there is no significant difference in the antioxygenic function when the concentration is changed from 0.02 to 0.1%. The studies made with the liquid paraffin system (Table V) tend to show that the deterioration of vitamin-A is due to the changes in the vitamin-A molecule, and this deterioration is inhibited to a considerable extent when an ester molecule with an antioxidant is present. It is apparent therefore that the unsaturation in the diluent in any vitamin-A preparation, as discussed previously by Basu (cf. *Ann. Biochem. Exp. Med.*, 1941, **1**, 165), is not the only cause of deterioration of the vitamin. On the contrary, vitamin-A in presence of an antioxidant is being found to be more stable on aeration in an unsaturated glyceride or an ester system than in a liquid paraffin system. Further, from the fact that vitamin-A potency is maintained to the same degree in the saturated or unsaturated glyceride or ester system in presence of an antioxidant, the question arises whether the glyceride (natural or artificial) as well as the ester molecule plays a role in helping the antioxidant in inhibiting the onset of oxidation in the vitamin-A molecule. Further work is in progress.

## DURABILITY OF SODA—LIME—SILICATE GLASSES. PART IV

By AMALENDRA CHOWDHURY AND H. N. DAS-GUPTA

A detailed study of the phenomenon of the tendency of the  $\text{H}_2\text{SO}_4$  value of glass powder to give lower  $\text{H}_2\text{SO}_4$  value after a few determinations on exposure has been made. The successive residual  $\text{H}_2\text{SO}_4$  values of chilled glass is found to be distinctly higher than the corresponding values for the same glasses after annealing.

In part I of this series of papers it was pointed out that if the glass powder, left after the determination of sulphuric acid value, be kept exposed to atmosphere under moist condition, it again gave sulphuric acid value of a lower magnitude (this *Journal*, 1947, **24**, 477). Again, in connection with our study of the effect of annealing on chemical durability of glass, it has been found that the above tendency is also more or less pronounced, depending, however, upon the thickness of the glass mass and the total surface exposed by it (Sen, Chowdhury and Das-Gupta, *ibid.*, 1949, **26**, 353, 379). The present paper embraces a detailed study of the above observed phenomenon.

From the experimental portion it will be evident that soda-lime-silicate glass, whether chilled or annealed, when subjected successively to powder test (Puddle, *J. Soc. Glass Tech.*, 1920, **4**, 3, 299), after intervals of 24 hours each, gives sulphuric acid values of descending magnitude and up to a restricted number of times. In order to avoid confusion, these values have been designated as residual sulphuric acid values. On an average, nine or ten such treatments are necessary, when the last residual sulphuric acid value becomes almost zero. From a comparative study, it is found that the successive residual sulphuric acid values of chilled glasses are distinctly higher than the corresponding values for the same glasses after annealing (Table II).

The effect of successive heat treatments on soda-lime-silicate glass is also interesting. Thus, the annealed glass powder, which ceases to give residual sulphuric acid value, if it be again subjected to annealing temperature for a specified time and then cooled slowly, it gives a series of residual sulphuric acid values. If this be repeated a number of times, different series of residual sulphuric acid values are obtained (Table IV). In each case, however, the annealing was done at  $500^\circ$  for five hours.

### EXPERIMENTAL

In order to get measures in respect of successive residual sulphuric acid values, two different series of 'like' glasses were prepared. These glasses were founded and plained as usual in Morgan crucibles. In each case the glass was chilled rapidly so as to avoid the favourable effect of slow cooling. Table I shows the purity of the ingredients used, and Table II, the % composition of the batch mixtures. Each specimen was

subjected to powder test and the residual powder was allowed to remain moist and exposed to atmosphere in a glass case for 24 hours. This was again heated with distilled water (100 c.c.) at  $80^{\circ}$  for an hour. The liquid was then filtered and the residue thoroughly washed with distilled water, the runnings being added to the filtrate. The filtrate was titrated, as usual, with sulphuric acid and the residual glass was again kept exposed to atmosphere under identical conditions for 24 hours. The exposed product was next treated with water as above. Operations like alternate exposure and water digestion were repeated a number of times, till the powders ceased to give any residual sulphuric acid value. These results have been included in Table III.

TABLE I

Material.	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO.	MgO	Na <sub>2</sub> CO <sub>3</sub>	NaCl, etc.	Loss
Sand	98.9%	0.2%	0.2%	Slight trace	Slight trace	...	...	0.5%
Lime ...	3.1	0.9	2.1	75.3%	0.2%	...	...	...
Soda ash		—		Slight trace	Slight trace	96.6	Slight	3.1

TABLE II

Series	Batch No.	Percentage composition		
		SiO <sub>2</sub>	Na <sub>2</sub> O	CaO
A	1	73	15	12
C	17	74	16	10

TABLE III

Batch No.	Condition of glass.	S.A.V	Duration (in days) after which the residual H <sub>2</sub> SO <sub>4</sub> values determined											
			1	2	3	4	5	6	7	8	9	10	11	12
1	Chilled	279.8	118.5	99.6	72	44.4	32.7	21.6	11.6	7.9	2.3	0.8	Nil	Nil
	Annealed	235	116	60.5	41.6	35.3	15.1	12.6	8.2	4.1	0.5	Nil	Nil	Nil
17	Chilled	582	175.1	81.4	69.3	51.9	40.3	31.1	18.5	12.7	9.6	2.7	0.9	Nil
	Annealed	506	167.3	72.6	56.4	42.3	34.3	26.2	16.1	10.3	3.5	1.2	Nil	Nil

It is thus evident from Table III that in each case, the tendency towards giving residual sulphuric acid value ceases after the lapse of 11 days. Prolonged exposure does not exert any opposite effect. This was tested with two samples (No. 1, annealed and No. 17, chilled), obtained on the 12th day. Each was exposed moist for a further period of one month. No positive result could be obtained in any case.

In order to follow the effect of repeated heat treatments on glass, the residual powder (batch No. 17, annealed), obtained on the 12th day, was again annealed at 500° for 5 hours. The annealed mass was subjected, as before, to powder test for a number of successive days, till the residual sulphuric acid value was nil. In each case the interval between any two experiments were exactly 24 hours. The powder was again annealed and the determination of residual sulphuric acid value was continued. This was continued for 2 months and the results have been incorporated in Table IV.

TABLE IV

Duration (days).	Residual S. A. V.	Duration (days)	Residual S. A. V.	Duration (days).	Residual S. A. V.
13	*	29	2.1	45	*
14	127	30	†	46	28.2
15	22.1	31	48.4	47	6.05
16	18.1	32	22.1	48	Nil
17	6.5	33	12.1	49	*
18	Nil	34	Nil	50	28.2
19	*	35	†	51	4.2
20	54.4	36	34.2	52	Nil
21	24.2	37	24.2	53	*
22	18.1	38	12.1	54	16.1
23	16.1	39	3.2	55	6.05
24	4.03	40	Nil	56	Nil
25	*	41	*	57	*
26	76.7	42	40.3	58	16.1
27	28.2	43	10.01	59	7.2
28	14.2	44	5.0	60	Nil

\* Indicates annealing. S. A. V. indicates sulphuric acid value.

## DISCUSSION

It is a fact that a chilled glass shows a distinctly lower resistivity than the same glass after annealing. It is considered that this increased durability is due to a structural change, which brings about strengthening of the bond between the alkali ion and the anionic network (Williams and Weyl, *Glass Ind.*, 1945, 26, 275, 325). From our findings, however, we cannot subscribe entirely to the above views. For, if annealing were

responsible for strengthening the forces which hold the alkali ions in glass, no residual sulphuric acid values should have been obtained. Secondly, there can hardly be any justification for the development of successive residual sulphuric acid values, when the glass is subjected to repeated heat treatments within the annealing temperature range. The problem becomes more complicated when it is found that there is an appreciable difference, in respect of durability, between the lump and the powdered glass from the same melt, although both may be annealed simultaneously under identical conditions. In the former case the sulphuric acid value is appreciably lower than that of the latter (Sen, Chowdhury and Das-Gupta, Part III, *loc. cit.*).

The tendency towards increased concentration of alkali at the surface is uniformly more with the powdered glass, and from Table IV, it will be clear that annealing tends to increase this tendency. This conclusion, then, is just the opposite of what has been stated above. It appears therefore that there are some other factors responsible for this different behaviour. It is proposed to put forward our views after we have collected further data in this line.

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APPLIED GEOLOGY, DHANBAD.

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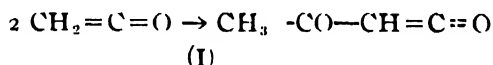


## ACYL KETENES AND THEIR POLYMERISATION

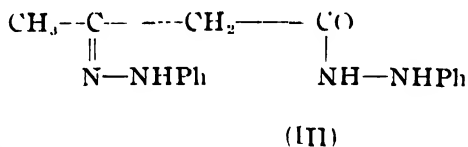
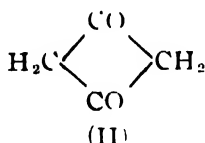
BY M. M. MAHALA AND S. S. DESHAPANDE

Reactions expected to give 2:4-diacylcyclobutane-1:3-dion (I) gave actually compounds of the class of dehydracetic acid (II). It is suggested that transformation of (I) into (II) takes place through acyl ketene as an intermediate.

By allowing ketene to polymerise at low temperature Chick and Willsmore (*J. Chem. Soc.*, 1908, **93**, 946) obtained a brown solid and a liquid in poor yield. The latter on fractionation boiled at 125°-127° and was found to consist of a compound  $C_4H_4O_2$  (M. W. 84) which, from its properties, was regarded by them to be acetylketene (I)

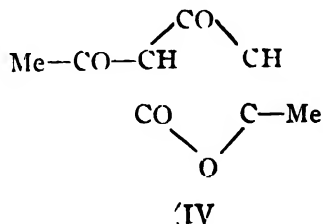


The isomeric cyclobutane-1:3-dion structure (II) was not preferred on ground of physical properties and of the fact that with phenylhydrazine the product obtained was phenylhydrazino-phenylhydrazide (III) instead of the diphenylhydrazone of the diketone (II).

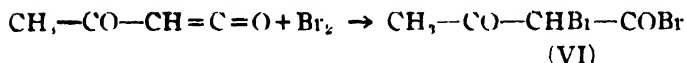
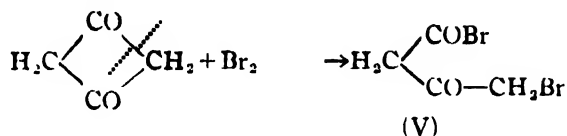


Staudinger and Bereza (*Ber.*, 1909, **42**, 4908) from the study of a disubstituted ketene, which they were investigating and which according to them polymerised to the corresponding cyclobutane-1:3-dion, suggested that Chick and Willsmore's 'acetyl ketene' was really cyclobutane-1:3-dion (II). The acetyketene structure was according to them further untenable on the ground that the compound, unlike ketene, was stable and did not add alcohol.

Chick and Willsmore (*J. Chem. Soc.*, 1910, **97**, 1978) in reply pointed out that in presence of a trace of mineral acid their compound gradually added alcohol and formed acetoacetic ester and that on prolonged standing in presence of alcohol, dehydracetic acid (IV) was the final product.

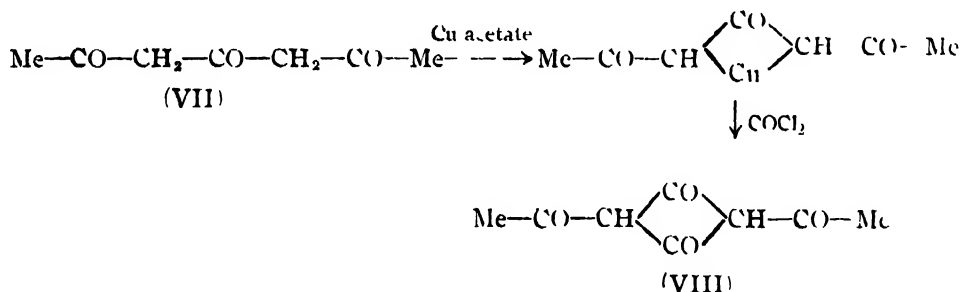


Since, however, the compound added bromine to form  $\gamma$ -bromoacetoacetyl bromide (V) and not the  $\alpha$ -bromo compound (VI)

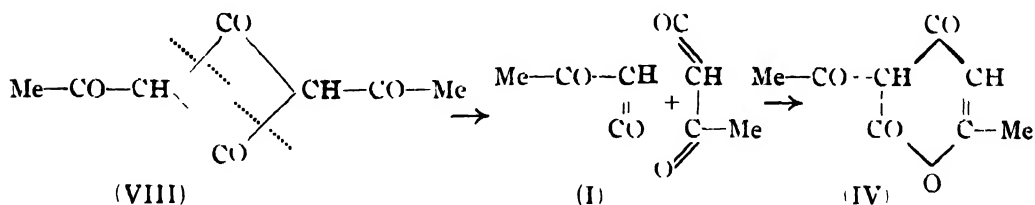


they modified their original view and accepted Staudinger and Bereza's *cyclobutane-1:3-dione* structure for their compound. They admitted that "the true acetylketone has therefore yet to be discovered, and when discovered it will resemble *cyclobutane-1:3-dione* in its reactions."

Billore, Nigam, Kaushal and Deshapande (this *Journal*, 1946, **23**, 19) attempted the synthesis of 2:4-diacetylcyclobutane-1:3 dione (VIII) by treating copper salt of diacetylacetone (VII) with carbonyl chloride in benzene



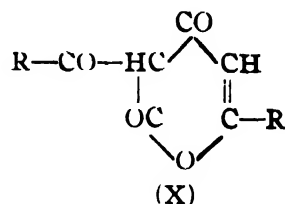
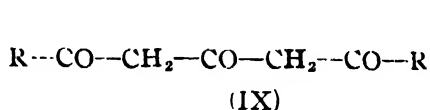
They obtained, however, a product which from its properties and analysis was identified by them as dehydracetic acid (IV). They suggested that on account of the instability of the structure (VIII) (cf. Ingold, *J. Chem. Soc.*, 1921, **119**, 305) fission took place into two molecules of acetylketene (I) which then recombined to form the more stable six-ring structure of dehydracetic acid.



The present work was undertaken to see whether more instances of this kind of transformation could be collected.

When the copper salt of dipropionyl acetone (IX, R = Et) (Deshapande, Dingankar and Kokil, this *Journal*, 1934, **10**, 595) was treated in benzene suspension with carbonyl chloride, dissolved in benzene, the sole product of the reaction was identified as dehydro-

propionylacetic acid (X, R = Et) (Pechmann and Neger, *Annalen*, 1893, 273, 86; Deshapande, this *Journal*, 1932, 8, 303)



The copper salt of di-*n*-butyrylacetone (IX, R = C<sub>3</sub>H<sub>7</sub>) (Deshapande, Dingankar and Kokil, *loc. cit.*) under similar conditions gave dehydrobutyrylacetic acid (X, R = C<sub>3</sub>H<sub>7</sub>) (Deshapande, *loc. cit.*).

It seems from the cases so far studied that when a reaction is expected to yield 2 : 4-diacylcyclobutane-1 : 3-dione, the compound actually formed belongs to the class of dehydracetic acid. The intermediate formation of an acylketene and its polymerisation to more stable six-ring structure is the mechanism suggested. The replacement of acyl by alkyl groups in 2 : 4-positions of cyclobutane-1 : 3-dione precludes the possibility of transformation of four-ring into six-ring in the manner suggested above. Thus, 2 : 4-dimethylcyclobutane-1 : 3-dione, obtained by decarboxylation of the 4-carboxylic acid (Schroter, *Ber.*, 1907, 40, 1607), is quite stable.

#### EXPERIMENTAL

*Copper Salt of Dipropionylacetone.*—Dipropionylacetone (prepared from 2 : 6-diethyl-4-pyrone by fission with barium hydroxide followed by acidification) was dissolved in alcohol. Cold saturated solution of sodium acetate and copper acetate was added to it when the green copper salt was precipitated which was washed free of copper acetate and was dried at 100°, yield almost the theoretical.

*Reaction with Carbonyl Chloride.*—To the suspension of the dry copper salt (5.7 g., 1 mol.) in dry benzene (30 c.c.) was added, under cooling, a solution of carbonyl chloride (2.6 g., 1 mol., liquefied at 0°), dissolved in benzene (18 c.c.). The reaction mixture was kept at 0° for 5 hours with occasional shaking; it was then allowed to remain at room temperature for five days for the reaction to complete. The deep brown benzene layer was filtered off from copper chloride, washed with water, dried and the solvent allowed to evaporate. The crystalline mass obtained was recrystallised from aqueous alcohol in needles, m.p. 71° (mixed m.p. with an authentic specimen of dehydropropionylacetic acid, prepared from dehydropropionylacetocarboxylic acid, 71°; Pechmann and Neger, *loc. cit.*), yield 2.5 g.

The copper salt of di-*n*-butyrylacetone was prepared from the ketone and was treated with carbonyl chloride in the same manner as the copper salt of the lower homologue. The copper salt (7.5 g.) and carbonyl chloride (2.9 g.) were used. The red benzene layer after completion of the reaction was filtered from copper chloride, washed with water and extracted with caustic soda. On acidifying the aqueous layer, a liquid separated which was extracted with ether. On washing and drying the ethereal extract

and removing the solvent, a liquid with acid reactions remained (yield 3 g.). After cooling by ice the liquid solidified. The solid, freed from little adhering liquid by draining, melted at  $16^{\circ}$  (dehydrobutyrylacetic acid freezes at  $16^{\circ}$ ). As mixed melting point observations at such low temperature are not convincing, confirmation of the identity of the acid with dehydrobutyrylacetic acid was obtained by determination of its equivalent weight. (Found : Equiv., 227  $C_{12}H_{16}O_4$  requires equiv , 224).

CHEMICAL LABORATORIES,  
AGRA COLLEGE, AGRA

*Received June 7, 1949.*

SIR PRAFULLA CHANDRA RAY  
MEMORIAL LECTURE \*

BY BIMAN BIHARI DEY

I consider it a great privilege to be invited to deliver the Sir Prafulla Chandra Ray Memorial Lecture this year, and my best thanks are due to the Council of the Indian Chemical Society for this honour.

Five years have rolled away since the great savant left this world, full of years and honours. To many of you of the younger generation to-day, he is perhaps only a slowly fading memory, but to those of us who had the privilege of intimate association with him in the early formative years of our lives, he would never cease to be our *Guru* and preceptor, for, in our innermost thoughts and actions even now, particularly when we are in doubts or difficulties, our minds turn unconsciously to him, thinking of how our Professor would have reacted to such and such situations in life, and in many an emergency we still seek light and guidance from him.

It was in July 1906, more than 43 years ago, that I had the first opportunity of coming into contact with Professor P. C. Ray, sitting at his feet as one of his pupils in the third year B.Sc. classes of the Presidency College, Calcutta, under the old regulations of the Calcutta University. To us, freshmen, in those early days of our career, everything in the College seemed to be awe-inspiring: from the imposing buildings, the wide staircases and corridors, the large laboratories in the innermost recesses of which some wizard, we were told, was trying to change copper into gold, or another trying to prove that plants had the same feelings and impulses of pleasure and pain, of joy and sorrow, and responded to stimuli in the same way as animals, to the elegant lecture theatres, and libraries, and, last but not the least, the dignified Professors who seemed to walk at a great height and distance from us. But, in a short time I was aware of a feeling—and this was perhaps the experience of many of my fellow students—that there was at least one of them who had come closer and established a sort of personal contact with me, and this was no other than the Professor of Chemistry. This was the unique characteristic of Professor P.C. Ray—he never kept his students at a distance, but admitted them very soon into the intimacy of his thoughts and even of friendship. His lectures were never laboured, nor did he seek to make them erudite, but they were always punctuated with good experimental demonstrations, and his simple talk was full of homilies and illustrations from life, intended to drive home to us, beginners, the elementary laws of chemistry—the laws of chemical combination, decomposition, etc. On some days, while discussing a topic in chemistry, he would suddenly make a digression to some of the social evils which were rampant in our society—they were probably rankling in his mind all the time, he having come across reports of a particu-

\* Delivered under the auspices of the Indian Chemical Society on August 2, 1949 at Calcutta.

larly bad case in the morning papers that day—the evils of the caste system, of untouchability, of early marriages of immature youths and maidens, of systems of extorting dowries from the poor parents of girls, and so on. He would warm up while speaking on what he called blots on our society and make apt quotations often full of satire, bearing on these problems from the poems of Tagore and other Bengali writers of the day. Our lecture in chemistry on that day would end with a sermon preached with eloquence, grace and humour for the benefit of his intimate circle of students, on whom, however, it never failed to create a deep and abiding impression. This was the essence of his philosophy as a teacher: He did not consider himself bound by the four walls of chemistry but like all true Gurus, he regarded his pupils as his children and his most intimate friends, entitled to share not merely his knowledge of the science of chemistry but his innermost thoughts and feelings on the burning problems of life as well. On other days again, he would be full of enthusiasm on a subject of research, which was immediately engaging his attention: it did not form a part of our course or curriculum, but syllabuses or curricula did not trouble him, nor deter him from unfolding before our enraptured gaze some of the secret methods of his researches. One such day I vividly remember: the rolls of the students attending the lecture had just been called as usual, by his assistant, when Professor Ray stepped into the class and shook before our eyes a small bottle containing what seemed to be some pale yellow crystals. With his inimitable jump of delight, he drew our attention to what he said was a new substance which he had been seeking for sometime, and which he had just then succeeded in preparing. He called it Silver-Mercuroso-Mercuric-Nitrate, explaining to us the method of its preparation and immediately proceeding to demonstrate the presence in the salt of the different silver, mercurous, mercuric and nitrate ions. These were some of the special features of Sir Prafulla's lectures to his junior classes. He drew the hearts of the boys out to him, which was undoubtedly the reason why they never found a moment of their hour with him dull or uninteresting.

As I look back upon those days of our studies at the Presidency College, Calcutta, with Dr. Jagadish Bose as the presiding genius of the Physics Department and Dr. Prafulla Ray, the presiding genius in Chemistry, memories of the past rush into my mind and I have a feeling—the present generation of students will, I hope, forgive me for cherishing this pride of contemporary times, a feeling that we had the good fortune of studying in that great Institution when it was at the pinnacle of its fame and glory. It was during our post-graduate studies, however, from 1908 to 1910 that we were thrown into the most intimate contact with our Professor. We were privileged to watch at close quarters the research experiments carried out by him and his assistants, and some of us were even permitted, particularly during holidays, to assist him in these researches. It was at this time that some of us were in the habit of visiting him occasionally in the evenings. Many were the delightful hours which we spent with him in conversations of absorbing interest in his austere little bedroom in the Bengal Chemical and Pharmaceutical Works office at 51, Upper Circular Road, Calcutta, where he resided in those days. On these occasions he would talk without reserve and tell us the fascinating story of his rich experiences in life, of his hopes and

fears, his joys and sorrows, of the numerous problems—educational and social, political and industrial—facing the people, and his high hopes about solving them with the help of his young students, whom he considered to be the spearhead of all progress in the country. The memory of those days, of the joyous aspirations and bright hopes raised in our young minds, can never be effaced or dimmed.

I do not wish to speak in detail on the various topics of researches in which Professor Ray had been engaged during his long career as a Professor of Chemistry. His researches on nitrites, particularly those of mercury, are now common knowledge and form the subject of text-books in chemistry. These researches covered roughly the period of two decades from 1892 to 1912. Many were the publications which found their way during this period from the chemical laboratories of the Presidency College to the Scientific journals of Europe and attracted the notice of such well known workers as Ramsay, Roscoe, Divers, Velej and others. From the elusive and unstable ammonium nitrite, which Professor Ray first prepared in the pure state, subliming the crystals in a vacuum and showing that the vapour had normal density, it was but the next step for him to proceed to prepare and study the stabilities of the alkyl ammonium nitrites, which were obtained by the double decomposition of alkyl amine hydrochlorides and silver nitrite in cold aqueous solution. It is very pleasant to recall the fact that my first apprenticeship at research under Sir Prafulla Chandra Ray began in 1910 on the preparation and thermal decomposition in a Sprengel vacuum of tetramethyl ammonium nitrite and tetramethyl ammonium hyponitrite. I would like to digress a little at this point from the main theme of this lecture and relate to you an incident of our early experience in the preparation of the starting material for this research—an incident which might almost have ended in a disaster. Tetramethyl ammonium nitrite required the preparation in the first instance of tetramethyl ammonium iodide, for which the only known method was the old Hofmann reaction between methyl iodide and liquor ammonia by heating under pressure in sealed tubes at steam temperatures. Our first experiment was entirely successful, although we were unaware of it, and, on opening the tubes, crystals were found to have separated from the cold liquid, shining like jewels. According to literature, however, these crystals were supposed to be mainly those of ammonium iodide and hence to be neglected, the tetramethyl ammonium salt being obtained only from the filtered liquid after boiling with potash to liberate the free trimethyl, dimethyl and methyl amines from their combinations with hydriodic acid, and then concentrating the liquid. I need hardly say that this procedure never yielded the material, and our repeated failures to obtain the desired compound led one day to a disastrous explosion in the laboratory, the loud report of which was heard throughout the building; the water-bath in which the sealed tubes were being heated had run dry while we were attending a lecture, and this led to the shattering explosion. The unfortunate accident drew on our heads the wrath and censure of the whole of the laboratory staff, of whom the chief and the most feared but respected member was the late Prof. Chandrabhushan Bhaduri. Fortunately for us this accident led eventually to the detection of our error in rejecting as ammonium iodide what was really slightly impure tetramethyl ammonium iodide which was later obtained pure after one or two

crystallisations from water. The interaction of this iodide with silver nitrite and silver hyponitrite in warm aqueous solutions gave the desired quaternary ammonium nitrite and hyponitrite.

It is with feelings of deep gratitude that I recall the great encouragement and help which I received from the Professor in my first attempt at independent research which was also on the subject of nitrites, viz., the interaction of hydrazine salts with nitrites, in which I had the valued collaboration of my late lamented friend, Dr. H. K. Sen. It may be of interest to my present audience to know that one of the methods for estimation of nitrites, which was very dear to our Professor, involved the use of the Crum Nitrometer, which used to be a most potent weapon in his hands in the prosecution of these researches. The nitrometer consisted of a graduated tube open at one end and with a stop-cock and a cup at the other end. This was filled with mercury and inverted in a trough of mercury, with the cup at the top. The solution of the nitrite (definite volume) was put into the cup and gradually introduced by opening the stop-cock carefully and finally washing it in with distilled water. A few drops of strong sulphuric acid were introduced from the bottom of the tube under the mercury trough when NO was given off which collected at the top of the nitrometer and its volume read off and corrected to N.T.P. It gave the most accurate results in our estimations of nitrites and was very frequently used by Professor Ray in his researches. The results of our work were published in the *Zeitschrift für anorganische Chemie* of April, 1911, and was reviewed in the Annual Reports on the Progress of Chemistry of that year. In August 1911 I sailed for England for studies in research in Organic Chemistry in the laboratories of the Imperial College—Royal College of Science, London, and the following summer (June, 1912) Professor Ray came to London as a delegate from the Calcutta University to the Empire Universities Conference, held in London that year. I might mention here an incident which illustrates better than anything else the sort of relationship which Professor Ray had with his pupils. I had no definite information about the date when Professor Ray was expected to arrive in London, or about the place where he was going to stay, but one day, early in June, as I was working in the morning in the laboratory, the laboratory-boy came to me with a card which I found to be that of Prof. P. C. Ray, saying that the gentleman was waiting outside. Professor Ray had ridden straight from the Victoria station to the Imperial College, knowing as it by instinct where he would get immediate help and relief, and he asked, nay, ordered me to take him straight to my lodgings! I mention this incident only to show the great love and trust which existed between Sir P. C. Ray and his pupils—a trust, which is so rare to find now-a-days. Then began a period of intimacy as between a *guru* and a *shishya*, when I had the privilege of acting as his friend and guide, escorting him to the various places which he wanted to visit and to the meetings which he had to attend, of acting as his amanuensis, and drafting his various letters and even nursing him at times when he became indisposed. I believe he addressed two Thursday evening meetings of the London Chemical Society on the subject of his researches on the “amine nitrites” which were specially attended by Professors Veley and Ramsay; the latter give him approbation at the end of his discourse, saying that Dr. Ray had almost singlehanded kept the torch of Science burning in that ancient land which was carried with acclamation by all the members



present. Our summer of 1912 in London was a memorable one, full of the happiest memories. Not only were there a number of distinguished personages from India, like Gokhale and others, whom we had opportunities of meeting quite often, but there was also our beloved poet Rabindranath Tagore, who came with his son and daughter-in-law and took up his residence in Alfred Place in South Kensington, very close to our club at 21, Cromwell Road. There was hardly a day without lectures, evening soirees, meetings and at-homes of some kind or other, and we the students threw ourselves wholeheartedly into the general excitement of the festivities to the detriment, perhaps, of our real work and studies.

It was my proud privilege to step into the shoes of Prof. P. C. Ray at the Presidency College, Calcutta on my return from England, when at the beginning of November, 1916, Professor Ray took a year's leave, preparatory to retirement, and joined the College of Science as the Palit Professor of Chemistry at the earnest request of the then Vice-Chancellor, the late Sir Asutosh Mookerjee. In those early days of severance of his connection with the Presidency College, Professor Ray's heart still remained in his old College, and on many an occasion, he would pay surprise visits to my laboratory and ask to be allowed to take up a part of my hour with the students to address them.

The *Magnum Opus* of Sir P. C. Ray's work may perhaps be considered to be the history of Hindu Chemistry on which he laboured for years with the help of several Sanskrit Pandits of Calcutta. It was published in two volumes, volume the first in 1902 and volume the second in 1908. A good portion of Volume II is taken up by a contribution on the positive sciences of the Ancient Hindus from the pen of the late Sir Brajendranath Seal who was then the Principal of the Victoria College, Cooch-Bihar, and who later went to Mysore at the invitation of the Maharaja to take up the post of the first Vice-Chancellor of the University of Mysore. The work has now become classical and attracted the attention of chemists all over the world. It is, I believe out of print and it is in the fitness of things that the Indian Chemical Society now is making an endeavour to publish a revised and enlarged edition of the book with a grant from the Central Government.

It is not my task to-day to make a comprehensive survey of the manifold activities of Professor Ray in the various fields of educational, scientific, literary and social work, and it will be difficult, even if I had the abilities for it to do so in the course of this lecture. I would, however, fail in my duty if I omitted to mention the fact that Professor Ray, though essentially a chemist, was no narrow specialist; he had wide sympathies and a rich and receptive mind full of intelligent appreciation of the beauties of art, literature and history, and he often used to take his students, particularly his research assistants and other advanced pupils to task for their neglect and ignorance of the humanities. In 1910 Professor Ray was elected President for the annual meeting of the Bangiya Sahitya Parishad, which was to be held at Rajshahi in Bengal, and I remember the enthusiasm with which he threw himself into the work of composing his Presidential Address, which created a deep impression on the literary circles in Bengal and received their homage and admiration. He has since written on many subjects, in numerous journals and magazines, has spoken from many platforms, and in times of emergency and crisis in the country has always been in the forefront in coming to the

rescue of his distressed fellow-beings. His "Impressions of a Bengalee Chemist", written in two volumes towards the end of his life, would bear testimony to his wide interests in life and his multifarious activities.

No estimate of the value of his contributions to the advancement of his countrymen would be complete which did not take note of his pioneering labours in the foundations of chemical industries in this country. The Bengal Chemical and Pharmaceutical Works are deservedly considered to be his direct offspring, but there are numerous others which are flourishing to-day, which his inspiring example and genius and encouragement helped in bringing into existence. He was never tired of exhorting his countrymen to take to industries and commerce and not hanker for jobs under Government, and he always held before the youths of the country the examples of men the world over who, through tireless industry and self-confidence, rose from small beginnings to the positions of industrial magnates, and who gave, as he did himself, their large earnings for philanthropic objects for the benefit of humanity.

It would be no exaggeration to state that the ambition to utilise scientific knowledge for the removal of the industrial backwardness and the consequent degrading poverty of the country was first kindled in many of us when we heard from his own lips the wonderful story of the growth of the Bengal Chemical and Pharmaceutical Works from a small beginning in the nineties of the last century, when he and a few friends scraped together about a thousand rupees out of their small savings for starting this concern, to its present stature of perhaps the premier chemical and pharmaceutical concern in India.

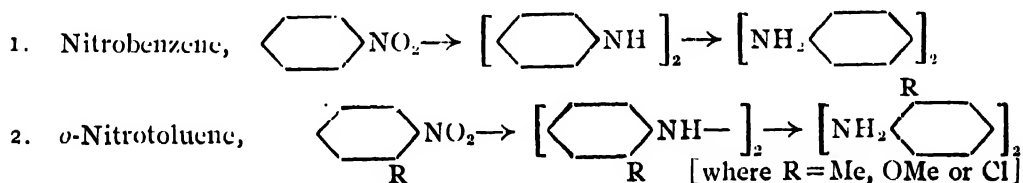
#### APPLICATION OF THE ELECTRIC CURRENT TO THE MANUFACTURE OF ORGANIC CHEMICALS

It would therefore be only appropriate, I believe, if I spoke to-day on one of these scientific industrial problems which I have been engaged in investigating lately, viz., the application of the electric current to the manufacture of certain organic chemicals of industrial importance—a subject of immense significance in the development of several basic industries of this country. Electricity enters to-day into the production of a large variety of basic materials, such as metals, alloys, chemicals and fertilisers, abrasives, etc. Many of these serve as raw materials for other industries. In some of these, the use of electricity is indispensable as in the production of aluminium, sodium, magnesium, calcium carbide, fused alumina, etc. while in others it is preferred to the chemical processes, as it leads to purer products and are often more economical. Organic products cannot of course compare in bulk and value with the inorganic products of electrochemical industries, but many of these find important uses as dye-intermediates, photographic developers and drugs. It is all the more regrettable therefore, that the subject of manufacture of organic compounds by electrolytic methods has not been given the prominence which it undoubtedly deserves. This is not because electrolytic methods have not been employed in organic industries—in fact, numerous applications have occurred—but, as Thatcher, one of the pioneers of technical electrochemistry in U. S. A., has said "it will probably be difficult, if not impossible, to cite another branch of applied science in which such extreme reticence has been maintained." The typical reactions of organic chemistry like reduction, oxidation and substitution may often be

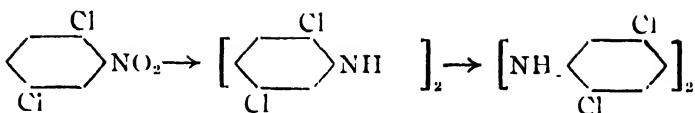
carried out with ease, if not with elegance, by electrolytic methods. Expensive reducing or oxidising agents, like zinc, tin, lead peroxide, chromic oxide, etc., are dispensed with and there are no sludges, therefore, of inorganic by-products to be removed. Once the right conditions for a particular desired result have been determined, the electrolytic method should be, and, indeed, has proved superior to the chemical method. A promising survey of the raw material position for the development of the dyestuff industry in India has been made by Pai and Venkataramanan (*Jour. Sci. Ind. Res.*, 1942, 1). The primary materials which are required, viz., Benzene, Toluene, Phenol, Naphthalene, etc., are available, or potentially available, in sufficiently large quantities, but these have to be converted into the intermediates like Naphthols and Naphthylamines, Aniline, Toluidine, Benzidine, etc. The application of electrochemical methods to the commercial production of such technically important compounds in India is a promising field which has been lying almost unexplored. Researches on the manufacture of certain special dye-intermediates like Benzidine, Toluidine, Dianisidine, Diphenetidine, etc. and of *para*-aminophenol, 2:4-diaminophenol, etc., and their analogues have been in progress for the past several years in the chemistry laboratories of the Presidency College, Madras, under the auspices of the Board of Scientific and Industrial Research. I shall speak to-day on the results of some of these researches which have proved beyond doubt that these intermediates, some of which have been produced in our laboratory on a pilot-plant scale, can be manufactured economically by electrochemical methods which are superior to the old chemical methods in ease of operation, purity of product and cost of production. I shall first relate the results obtained by us in the electrolytic reduction of aromatic nitro compounds in alkaline media, and then refer to certain interesting results obtained in the electrolytic reduction of aromatic nitro compounds in acid media.

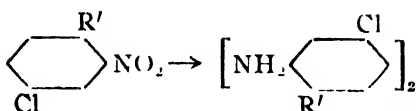
#### A. REDUCTION OF AROMATIC NITRO COMPOUNDS IN ALKALINE MEDIA

As is well known, the reduction of aromatic nitro compounds in alkaline media leads generally to the production of hydrazo compounds. The mechanism of this reaction is now well understood. The reaction occurs in stages, and in the presence of alkali, the nitroso and the hydroxylamino-bodies interact among themselves to give first the azoxy and then azo and then hydrazo compounds. The hydrazo-bodies do not have any intrinsic value themselves, but they owe their importance to the fact that on treatment with mineral acids, they undergo the "benzidine transformation" and form the diamines of the diphenyl series which are used extensively in the manufacture of certain valuable substantive cotton dyes. A study of the electrolytic reduction of the following seven aromatic nitro compounds has now been completed and the details have been published in *J. Sci. Ind. Res.*, 1946-1948.



3. *o*-Nitroanisole,4. *o*-Nitrochlorobenzene,

5. 2:5-Dichloro-2-nitrobenzene, 

6. 2-Nitro-1-chloroanisole, 

7. 2-Nitro-4-chlorophenetic. [where R' = OMe or OEt]

### 1. Nitrobenzene

The electro-reduction of nitrobenzene in alkaline media has been studied by numerous workers. Some of the more important of these only are cited here. Straub was one of the first to study the electro-reduction of nitrobenzene and took out a patent on this process (D. R. P. 79731 of 1891). He carried out the reduction in alcoholic caustic potash and claimed to have obtained hydrazo-benzene in a yield of 85%. Wulffing (D. R. P. 110234 of 1898) claimed an improvement by substituting sodium acetate for the caustic alkali, which led to lesser tar-formation and longer diaphragm life. On the laboratory scale, the method leads to good results; but, the use of alcohol on the technical scale has many disadvantages, the chief of which are loss of solvent by evaporation, high cell resistances, dilution of alcohol by flow of water from the anolyte, and last but not the least, the hazard of fire. Elbs (*Chem. Ztg.*, 1893, **17**, 209) suggested the reduction of nitro compounds without a solvent, the depolariser, *i.e.*, the nitro compound in this case, being maintained in a state of emulsion by stirring. Based on this idea, no fewer than 12 different patents have been taken out during the years 1900 to 1917. In some of these (Loeb, D. R. P. 116467 of 1900) the reduction is carried out in alkaline emulsion upto the azoxy-stage, the solution then acidified and reduction continued, leading to the production of benzidine in the electrolytic cell itself. In others (Meister, Lucius and Brunning, D. R. P. 127727 of 1900), the reduction is carried out on similar lines, but the diaphragm is dispensed with by the use of a small anode of iron. Sometimes again (Gesellschaft für chemische Industrie, D. R. P. 297019 of 1917), a diaphragm is dispensed with by conducting the reduction in a solvent like benzene, the cathode being set at the interface of the two layers and rotated at such a speed that neither a too fine nor too gross an emulsion is formed.

The methods outlined in these procedures involve either the use of a non-electrolytic solvent like alcohol or benzene, or the use of the depolariser in a state of emulsion by stirring. Later, it was found that concentrated solutions of salts of certain aromatic acids had good solvent properties and McKee and Gerapostolou (*Trans. Amer. Electrochem. Soc.*, 1935, **68**, 329) found that concentrated solutions of mixtures of sodium and potassium xylene sulphonates were excellent solvents for nitro compounds, and particularly suitable for employment as solvents in electro-reduction.

Our main objective in undertaking this work was to find out which of the several promising methods was suitable for large-scale reduction and the optimum conditions for operating the selected method.

(1) *Reduction in alcoholic solution.*—Experiments using 350 g. of the nitro compound were carried out. It was found that in order to prevent the azo and hydrazo compounds from being thrown out of solution due to the progressive dilution of the alcohol, it was necessary to add at intervals further quantities of alcohol. It also became obvious that the reduction demanded operation at uneconomical voltages. The method, therefore, was considered unsuitable for operating on the industrial scale.

(2) *Reduction in a saturated solution of sodium and potassium xylene sulphonates.*—In our attempts to reproduce the results of McKee and Gerapostolou, several defects were noticed in the operation of the method. These were (a) excessive diffusion of the catholyte into the anolyte even with dense alundum diaphragms, the sulphuric acid getting extremely dark and viscous, which increased the cell resistance, (b) deterioration of the xylene sulphonate solution both in conductivity and in solvent power by repeated use, (c) the large admixture (up to 20%) of azobenzene with the hydrazobenzene produced, even though a large excess of current had been passed, and the reduction conducted at as low a current density as 1 amp. sq. dm., (d) fairly high cell voltage: in a cell handling 4.5 litres of xylene sulphonate solution and 1 kg. of nitro compound and with dense alundum diaphragms, 8 volts were found necessary for passing 40 amps. on an effective cathode surface of 40 sq. dm. On the whole the view expressed by McKee and others on the great utility of this method for the large-scale production of hydrazo compounds could not be confirmed. It was found suitable for the production of azo compounds in good yields, but not of hydrazo compounds.

(3) *Reduction in alkaline emulsion.*—All the recorded information on the subject is in the form of patent specifications. A systematic study of the reduction of nitrobenzene in alkaline emulsion was therefore undertaken, the preliminary experiments being conducted at monel, lead and iron cathodes, the anolyte in all cases being a 30% solution of sodium hydroxide kept inside a porous cylinder. As a result of these experiments it was found that (i) nitrobenzene is reduced at a monel cathode to a mixture of hydrazo- and azobenzene, (ii) the addition of lead oxide carried the reduction to completion, less than 5% of azo compound being found in the end product, (iii) at a lead cathode more than 90% of hydrazobenzene and 4 to 5% of azobenzene were obtained—the addition of lead oxide was found unnecessary, but the cathode was corroded by the action of alkali to some extent and the dissolved lead redeposited in a loose form, (iv) at an iron cathode in the presence of lead oxide the yield of hydrazobenzene was the highest, about 93%, and the azobenzene was the lowest, about 3%, (v) the current efficiency of the processes was good, only 10 to 20% of excess current having to be passed over that required theoretically, (vi) the formation of a crust of hydrazobenzene which was deposited on the cathode and the diaphragm, was a drawback in the earlier experiments, but this was removed later by the addition of xylene at a suitable stage, which helped in the removal of hydrazobenzene and in carrying the reduction to completion.

These preliminary experiments showed that the reduction of nitrobenzene in alkaline emulsion was superior to the other methods, both from the point of view of ease of operation and yield and quality of the hydrazobenzene. A systematic study of the reduction of nitrobenzene in alkaline emulsion was next undertaken with special

reference to the following factors: influence of current density, concentration of alkali and of depolariser and of addition agents. Iron was selected as the most suitable cathode from the point of view of technical application on a large scale. A cell of a simple design was made in which the parts could be easily assembled and in which all the factors except the variable factor under study could be reproduced to the minutest detail. The description of the cell, as designed for the purpose, has been given fully in *J. Sci. Ind. Res.* (1946, pp. 564-565). This cell has been of great value in conducting related studies with other nitro compounds like *ortho*-nitrotoluene *ortho*-nitroanisole, etc.

A typical reduction was conducted as follows. The alkali of the specified strength was heated to boiling with the addition agent so as to dissolve the latter and introduced into the cell. The porous diaphragm was also filled up to the same level with 30% alkali. The current was passed at 20 amps. for about 15 minutes with heating, and when the temperature had reached 80°, the nitro compound was added. The reduction was carried out at the specified amperage, keeping the temperature at 80°. When 90% of the theoretical current had been passed, 200 c.c. of xylene were added and the reduction continued till the solvent layer was just colourless. In some cases where the colour was not completely discharged, the reduction was carried on till the solvent layer had a constant shade of colour. The alkali and xylene layers were withdrawn from the cell, separated, and any free alkali in the xylene layer neutralised by passing carbon dioxide. The xylene layer was then poured into acid for benzidine transformation. When 100 g. of nitrobenzene had been taken, the transformation was effected by pouring into 80 c.c. of HCl (*d* 1.16) and 150 g. of ice, stirring for 5 hours in the cold and raising the temperature during the sixth hour to gentle boiling. The pasty mass was then filtered and the residue washed with xylene to free it from azobenzene. The filtrate consisted of two layers, the aqueous layer containing benzidine hydrochloride and the xylene layer, azobenzene. The residue consisting of benzidine hydrochloride was converted into the insoluble sulphate by addition of the calculated amount of dilute sulphuric acid. The benzidine sulphate was filtered, dried and weighed. The acid filtrate from this was basified, steam-distilled to remove aniline, and the aniline estimated by the bromide-bromate method. The azobenzene was recovered from the xylene layer by blowing in steam and removing the xylene.

In interpreting the results, some important points must be borne in mind :

(i) *Influence of current density.*—Since satisfactory yields of hydrazobenzene were obtained only by the addition of lead oxide, all the experiments on the influence of current density were conducted only after the addition of this compound. The lead oxide was first dissolved in the catholyte forming sodium plumbite. On passing the current, lead was deposited on the cathode in a spongy state. Since it was not possible to compute the exact surface offered by the spongy lead, only the surface offered by the cathode was taken into account. In any case, it can be assumed that the surface offered by the spongy lead will be a constant factor in all the experiments, provided that the same amount of lead oxide had been added.

(ii) *Influence of concentration of alkali.*—Current efficiency is not appreciably affected by increasing the alkali strength. There is a definite improvement in the material yield.

(iii) *Influence of concentration of depolariser.*—There is no marked improvement in current efficiency by increase of depolariser concentration. Material yield, is, however, definitely improved by increase of depolariser concentration. On the technical scale the increased cell voltage due to increase of depolariser concentration may be a disadvantage.

(iv) *Influence of added compounds.*—Lead oxide is the most valuable addition agent. At the end of the reduction, lead is completely absent in the alkali layer. In technical operation, after completion of one reduction and withdrawal of the charge, a fresh charge can be added and the reduction continued without addition of any fresh amount of lead oxide, since the spongy lead from the previous reduction is almost completely retained in the cathode chamber.

The reason for the increased formation of hydrazo compound by the addition of lead oxide seems to be due to increased overvoltage when the metal is deposited on the cathode. In addition, because of the large surface area offered by the lead sponge, more intimate contact between the cathode and depolariser is favoured, so that rapid reduction can occur.

From the experimental data presented above, it has been proved that electrolytic reduction of nitrobenzene in alkaline emulsion at an iron cathode is probably superior to all other methods for the production of benzidine and is very suited for adoption on the industrial scale. The yield of benzidine obtained is nearly 90% of the theoretical and is about equal to that obtained by Pietz David ("Fundamental Operations of Dye Chemistry", 1927, p. 60) by chemical methods or that obtained in reduction with sodium amalgam or that claimed for the electrolytic method stated to be in operation in Switzerland (Fichter, Congress International of Electricity, Paris, Section I, Rapport No. 19, 1932, p. 6).

A study of the process on a pilot-plant scale was undertaken to study fully the economic aspects of the process. At first the reductions were conducted in a cell handling 2 kg. of nitrobenzene, with a cathode surface of 10 sq. dm. and operated at 100 amps. and then in a cell handling 10 kg. with cathode surface of 200 sq. dm. and operated at 450 amps.

As in the small-scale experiments described previously, the vessel of sheet iron itself served as the cathode chamber. Due to the difficulty of getting iron gauze, additional cathode surface was provided by a set of sheet iron vanes. An oval vessel was preferred to ensure a more uniform distribution of current. Instead of using a single anode set in a large central cylindrical diaphragm, three anodes in three smaller cylindrical diaphragms, arranged along the longer axis of the vessel, were employed. This was helpful in distributing the current evenly, avoiding overheating and in lowering the bath voltage.

The hydrazobenzene formed in the reduction was removed by xylene as in small-scale experiments and the large cell was operated with the same ease and smoothness as the small cell. No undesirable heating effects were noticed even with the large current and the cell was maintained at 80° quite easily by regulating the flow of water in the jacket. The only attention needed was to withdraw the weakened anolyte

at intervals of about six hours, fortify it to 20 to 25% and return it to the anode chambers, a process requiring only a few minutes each time. In an industrial cell, this operation may quite easily be made automatic by the regulated addition of solid caustic soda, so that there need be no interruption during the reduction. In an industrial electro-organic reduction, the unit cells are rarely operated at more than 1,000 amps., and large amounts are handled by multiplying such units, each carrying not more than 1,000 amps and increasing the duration of reduction as required. Our pilot plant, operated at 450 amps., can therefore furnish a fairly accurate idea of the operational features of the industrial cell. It is seen that the results obtained in the small-scale experiments are reproducible on the pilot-plant scale, both with regard to current and material yields. The process of electro-reduction of nitrobenzene in alkaline emulsion can therefore be considered technically sound and suitable for adoption on the industrial scale.

### 2. *o*-Nitrotoluene

References to the electrolytic reduction of *o*-nitrotoluene are contained in patent specifications (cf. Brunner, E.P. 15750, 1915).

In the electrolytic reduction of *o*-nitrotoluene, our studies were restricted to reduction at an iron cathode.

The most disturbing feature in all the reductions is the large proportion of toluidine which is simultaneously formed with the hydrazotoluene (cf. Diffenbach, D.R.P. 197714, Friedländer, 9, 112). It appears difficult to suppress amine formation to any appreciable extent. However, according to Löb (*Z. Elektrochem*, 1904, 10, 582), by proper adjustment of the cathode potential any desired product can be formed. The cathode potential should be held at such a level that reduction does not proceed beyond the phenylhydroxylamine stage. When all the phenylhydroxylamine derivative is used up in forming the azoxy compound by condensation with the nitroso compound, the cathode potential can be raised to a level where reduction of azoxy to hydrazo compound can take place. It is difficult to say how far this is practicable on a technical scale. Amines like toluidine or anisidine, are, however, not without value and their simultaneous formation along with hydrazo compounds need not render the electrolytic method for the production of the diamines unsound technically.

In a standard reduction, a little over 56 g. of hydrazotoluene was formed for every 100 g. of *o*-nitrotoluene reduced. With an 85% yield in the conversion, this ought to give nearly 70 g. of toluidine sulphate, but only 53 g. of toluidine sulphate were obtained.

### 3. *o*-Nitroanisole

The electrolytic reduction of *o*-nitroanisole in alkaline emulsion has not so far been reported. The reduction was therefore studied with reference to the following factors: influence of catalysts, current density, concentration of alkali and of depolariser. From the results obtained the following conclusions were drawn:



(1) At an iron cathode the reduction does not proceed to an appreciable extent beyond the azoxyanisole stage and anisidine is formed in large amounts as a by-product.

(2) The most satisfactory catalyst is lead monoxide leading to the highest yield of hydrazoanisole.

(3) Zinc oxide leads to more of anisidine being formed and a marked inhibition of reduction to the hydrazo stage.

(4) The addition of tin oxide takes the reduction to completion and there was hardly any azo or azoxy bodies in the reduction products but anisidine preponderates over the hydrazo body as in the previous cases.

(5) Ceric sulphate or vanadium pentoxide are of no value in increasing the yield of hydrazoanisole. In the presence of these compounds, the main products are anisidine and a mixture of azo- and azoxyanisole, hydrazo formation being negligible.

Since lead oxide was indispensable for the production of the hydrazo compound in good yields, the studies relating to influence of the rest of the factors were conducted only with the addition of this agent. The following conclusions were drawn from the results:—

(1) There is no appreciable diminution in anisidine formation by operating at a lower current density.

(2) There is no definite improvement in the yield of hydrazoanisole by increasing the concentration of alkali above 10%.

(3) By operating with a depolariser concentration of one to four volumes of alkali, the dianisidine is obtained in the highest yield; nearly 80% of theoretical. As in the case of the reduction of *o*-nitrotoluene, it does not seem possible to reduce the formation of amine to any considerable extent by the alteration of conditions. Since anisidine is also of value as a dye-intermediate, its production simultaneously with hydrazoanisole need not be considered as an objection to the application of the electrolytic method on a large scale.

The standard method of procedure for the reduction and isolation of products has been used. Yield of hydrazoanisole (m.p. 102°) was 72.1% of theory, and *o*-anisidine, 22% of theory. Yield of Dianisidine or 3:3'-dimethoxybenzidine (m.p. 135°) on conversion of hydrazoanisole was 90%.

#### 4. *o*-Nitrochlorobenzene

The reduction of *o*-nitrochlorobenzene was conducted on the basis of results obtained from earlier studies, employing lead monoxide as addition agent, a depolariser concentration of one to four volumes of sodium hydroxide and a low current density, such as 1 amp./sq. dm. It was seen that the preparation of *o*-dichlorohydrazobenzene in nearly 85% yield was possible by employing the above conditions, the current efficiency also reaching a high value. The hydrazo compound is obtained in a state of high purity, melting sharply at 87°, and is almost colourless.

The most noteworthy feature about *o*-dichlorohydrazobenzene is its extraordinary

stability in air and resistance to the "benzidine change" as compared to hydrazo-toluene or hydrazoanisole. It was only after employing 10 mols. of 50% sulphuric acid, that the "benzidine change" could be effected in a yield of 91.5% of the dichlorobenzidine.

*Ortho*-or 3:3'-dichlorobenzidine can therefore be prepared in an overall yield of more than 80% by the electrolytic reduction of *o*-nitrochlorobenzene in alkaline emulsion.

#### 5. 2:5-Dichloro-1-nitrobenzene

The study of this reduction was also restricted mainly to a few specific conditions. It was found that other conditions being equal, increase in the strength of the alkali employed caused an increase in the yield and in the current efficiency. This is probably due to better emulsification obtaining with alkali of strength approximating to that of the nitro compound. The best improvements in yields as well as the current efficiency are realised by operating with lower current density of 1 amp./sq.dm. and with a depolariser concentration of one volume to four volumes of catholyte. These would appear to be the optimum conditions for the preparation of tetrachlorobenzidine.

2:2':5:5'-Tetrachlorohydrazobenzene is a light yellow solid (m.p. 123.5°). Its stability in air and resistance to the benzidine transformation are even more marked than that of 2:2'-dichlorohydrazobenzene. Prolonged boiling with a larger excess of concentrated hydrochloric acid has to be carried out before it can be completely converted into the benzidine. Tetrachlorobenzidine has been prepared in this way, in a yield of nearly 85% as a grey powder, which crystallises from alcohol in orange-yellow flakes melting at 137.5°. It is a very feeble base and its salts, like the hydrochloride or sulphate, are immediately hydrolysed to the free base by the addition of water. The diacetyl derivative, crystallised from acetic acid, forms colourless needles (m.p. 297°) and the dibenzoyl derivative also crystallised from acetic acid in colourless needles (m.p. 250-52°). 3:3':6:6'-Tetrachlorobenzidine has been obtained also by purely synthetic means as described by Dey *et al.* to confirm the identity of the electrolytic product.

#### 6. 2-Nitro-4-chloroanisole

There is no reference in literature to the electrolytic reduction of 2-nitro-4-chloroanisole in alkaline medium.

Since the melting point of 2-nitro-4-chloroanisole was 98-99°, and the reduction was carried out generally at 80°, the nitro compound had to be kept in solution in 100 c.c. of benzene in the electrolytic cell. The following conclusions were drawn from a set of experiments conducted in order to arrive at the most favourable condition for the formation of the dichlorohydrazoanisole:

(1) Lead oxide is an indispensable catalyst for the production of dichlorohydrazoanisole.

(2) The formation of chloroanisidine in appreciable amounts (12 to 20%) is unavoidable.

(3) An increase in the concentration of the alkali (from 10 to 30%) results in increase in the yield of amine and a consequent decrease in the yield of the hydrazo compound.

(4) A current density of 1 amp./sq. dm. and a concentration of 10% sodium hydroxide while employing an increase depolariser concentration of 120 g. in 387 c.c. of the alkali gives the best yield of the hydrazo compound and reduces the amine formation to a minimum.

*Dichlorohydrazoanisole* (71.7% yield) is a light yellow solid (m.p. 116°) which turns deep orange when exposed to air, probably due to oxidation to azo compound. When treated with acids it undergoes the "benzidine transformation" readily to give 3:3'-dimethoxy-6:6'-dichlorobenzidine (m.p. 170-71°). 4-Chloro-*o*-anisidine (m.p. 80-81°) occurs as a side product to an extent of 16.2%.

#### 7. 2-Nitro-4-chlorophenetole

Neither electrolytic nor chemical reduction of this nitro compound to its hydrazo derivative has been reported so far in literature. Conditions similar to those worked out in the case of the preparation of allied compounds were applied in the present instance, but the yield of the hydrazo compound was relatively poor and the product was invariably contaminated with appreciable quantities of the corresponding azo and azoxy derivatives. Apart from the chlorophenetidine that is simultaneously produced, there is evidence also for the formation of other by-products, one of which appears to be a phenol. In this reduction also, a solvent had to be used. Instead of benzene, xylene was employed owing to its better solvent action on the products.

The crude dichlorohydrazophenetole obtained in a yield of 70 to 72% is an orange-yellow solid which turns deep orange on exposure to air, probably due to oxidation to azo compound. On crystallisation from xylene, it separates as bright yellow needles (m.p. 152°). In regard to the "benzidine transformation" of the hydrazo compound, despite several attempts at variations of the general method of boiling with mineral acids, the conversion did not exceed 64% of theory and to effect this, both concentrated hydrochloric acid and dilute sulphuric acid were found to behave equally well.

#### B. REDUCTION OF AROMATIC NITRO COMPOUNDS IN ACID MEDIA

The cathodic reduction of aromatic nitro compounds in acid media leads to a variety of products, the course of the reduction being to a large extent conditioned by the strength of the catholyte, the influence of the electrode material and the presence or absence of addition agents in the electrolyte. In dilute acid solution or suspension, according to Haber (*Z. Elektrochem.*, 1898, 4, 506), a nitro compound reduced at cathodes having a low overvoltage, such as platinum, yields a mixture of amine, aminophenol, azoxybenzene, azobenzene and benzidine. At high overvoltage

cathodes like those of lead, tin, mercury and zinc, although the reduction leads mainly to the production of amines, the presence of addition agents is said (D.R.P. 295841, 1915) to give good yields of aminophenols too. The aminophenols, however, occur in larger yields when the reduction takes place at a low overvoltage cathode in strongly acid media (Gattermann *et al.*, *Ber.* 1893, **26**, 1844; 1894, **27**, 1927; 1896, **29**, 3024). The bulk of the previous work in this field had related to the electrolytic preparation of amines, with perhaps the sole exception of the case of nitrobenzene, where conditions for the reduction to *para*-aminophenol had been studied by several workers (Noyes and Clement, *Ber.*, 1893, **26**, 990; Caeser, *Trans. Amer. Electrochem. Soc.*, 1927, **52**, 95). A systematic study was therefore undertaken on the electrolytic reduction of a series of aromatic nitro compounds, keeping in view our object of getting the maximum yield of the aminophenol and a minimum of the amine. Nitrobenzene was the first compound to be investigated and it was later followed by studies on the reduction of *ortho*- and *meta*-nitrotoluene, *m*-dinitrobenzene, *m*-nitroaniline, *o*-nitrochlorobenzene and *o*-nitrophenetole on the same lines; the results obtained have been the subject of several publications (*J.Sci. Ind. Res.*, 1946, **5**, 574; 1947, **6**, 83; 1948, **7**, 107, 113 etc.). Apart from developing suitable methods for the production of aminophenolic compounds, these investigations have resulted in certain observations of general interest. They have made it clear for example, that the overvoltage effect, varying from electrode to electrode, is by no means the only factor which controls the course of these reductions. There is also the catalytic influence of the cathode material, as distinct from its overvoltage effect, which has not so far been studied with a view to apportioning the relative influence of each of these on the course of the reactions.

Gattermann (*loc. cit.*, *Ber.*, 1893, etc.) was the first to describe the electrolytic preparation of aminophenolic compounds by the reduction of aromatic nitro compounds in acid media; he used warm concentrated sulphuric acid as the catholyte and platinum as electrode metal. Since Gattermann's classical experiments, several modifications have been reported by way of patent specifications (Darmstadter, D.R.P. 150800, 1901, etc.) and other literature, specially in regard to the electrolytic preparation of *p*-aminophenol. In fact, during the war of 1914 to 1918, several tons of *p*-aminophenol were manufactured by Thatcher's modification of the Gattermann procedure, substituting carbon electrodes for the platinum, and also by Eastman Kodak by another modification of the same procedure (See McDaniel, Schneider and Ballard, *Trans. Amer. Electrochem. Soc.*, 1921, **39**, 441).

Most of these improvements as well as those that followed later (e.g. those of Darmstadter, Burwell, Shoji, Brigham and Lukens, Altpeter and Khirkhgof) were aimed to lessen the rigour of the operating conditions in the Gattermann procedure by the use of less concentrated sulphuric acid and also replacement of the expensive cathode by less costly material. The mechanism of the formation of *p*-aminophenol by the electro-reduction of nitrobenzene is well understood. The  $\beta$ -phenylhydroxylamine molecule, formed initially by the reduction of nitrobenzene, rearranges itself in the presence of strong acid to *p*-aminophenol. The  $\beta$ -phenylhydroxylamine is also a good depolariser and can be further reduced to aniline at the cathode. The relative amounts of aniline and *para*-aminophenol will therefore depend on the relative speed

of rearrangement of the phenylhydroxylamine molecule and of its reduction to aniline. If therefore the reduction of phenylhydroxylamine to aniline could be retarded, higher yields of *para*-aminophenol might be expected. It has been suggested that this could be achieved by the addition of anti-catalysts or by the use of alloy electrodes.

The most rational approach for evolving a technical method appears to be on the lines suggested by Imray (E.P. 18081, 1915) by the use of anti-catalysts, and it is therefore surprising that no work has been carried out on the basis of these ideas. In almost all the reductions studied, maximum aminophenolic formation takes place in a catholyte of 20 to 30% sulphuric acid in the presence of suitable addition agents. In the case of *m*-dinitrobenzene and *m*-nitroaniline, however, although somewhat satisfactory yields were obtained at these dilutions, better yields resulted when a 40% sulphuric acid solution was employed as catholyte. The cathode material for these reductions consisted of lead, copper, monel or nickel at all of which under the conditions of the experiment, both aminophenols and amines were produced. Amongst these, copper and monel were found to be the most suitable cathode materials.

Mercury being a metal of high overvoltage, should, according to the accepted principles, have not only facilitated the reduction of the nitro compound to the hydroxylamine but also carried it further to the amino stage, giving little time for the hydroxylamine derivative to undergo isomerisation or enter into side-reactions. The experimental evidence seems, however, to show that the contrary is the case. Instead of reducing the hydroxylamine further to the amine stage, the mercury definitely helps in accelerating the speed of isomerisation to the aminophenolic compound, even in a comparatively dilute acid medium. This peculiar role of mercury is played by copper also in the status of cathode material, since reductions in the presence of its salt or otherwise have, in many cases, led to an increased yield of the aminophenol.

When mercuric sulphate is added to the catholyte and the reduction conducted in the usual manner, the cathode (copper or monel) is deposited with a shining surface of mercury. It was therefore considered to be of interest to examine if these results could be reproduced by using cathodes pre-coated with a mercury surface without further addition of mercuric sulphate. In the case of nitrobenzene pre-amalgamation of the cathode was observed to have the same effect as addition of mercuric sulphate, while in the cases of *o*- and *m*-nitrotoluenes and of *m*-nitroaniline, pre-amalgamation led to even greater reduction and to better yields of the aminophenols than when mercuric sulphate was used along with an unamalgamated cathode.

Another interesting fact that was observed in the course of studies of these reductions was the effect of copper sulphate added to the catholyte. The finely divided copper seems to play, as already indicated, the same role as that of mercury, and when copper sulphate was used in conjunction with amalgamated cathodes, relatively good yields of aminophenols and small yields of amines resulted. As regards the extent of reduction, in most cases, substantial improvements could be noticed. These results do not permit any definite conclusions being drawn as to which of the two, mercury or copper, acts as a better catalyst, in speeding up the isomerisation of the hydroxylamino derivative.

## E X P E R I M E N T A L

For all the reductions, the current was supplied from a dynamo with an output of 100 amps. at 6 volts. The anodes were in all cases made of lead and consisted of cylinders 1" in diameter and 2" in height. The anolyte was sulphuric acid of the same strength as the catholyte. It was found necessary to change the anolyte during the experiment, in certain cases, where the voltage rose to above 7 volts, but generally in all the reductions, the voltage was maintained between 4 and 7 volts. The materials of the cathodes experimented with were those of copper, monel, nickel and lead. The diaphragms used were those of German biscuit porcelain specially resistant to acids, 5" high and 2.5" in diameter. The working up of the products in the case of the reduction of nitrobenzene, *o*- and *m*-nitrotoluene, *o*-nitrochlorobenzene and *o*-nitrophenetole was as follows. At the end of the reduction, the acid solution is steam distilled to remove the nitro compound remaining unreduced and then filtered to remove insoluble matter through a glass sintered funnel. The acid solution is then neutralised carefully with a strong solution of soda ash till the solution just turns red litmus blue. Sufficient acid is then added to make the solution just turn blue litmus red. A few c. c. of a saturated solution of sodium bisulphite are then added and about 50-100 g. of decolourising charcoal. The mixture is then steam-distilled to remove the amine. *It is absolutely necessary at this stage that the mixture should not be even slightly on the alkaline side. The purity of the product obtained depends entirely on this.* The distillate is worked up for the amine. The hot solution is filtered from the charcoal and the pale yellow filtrate left overnight, preferably in the refrigerator, where the major portion of the aminophenolic body crystallises out and is filtered and dried. The mother-liquor is concentrated *in vacuo* in a stream of hydrogen, the concentration being stopped at the point when inorganic materials start separating. The solution is cooled, filtered and the residue washed with a small amount of water containing sodium bisulphite. The aminophenolic compound thus obtained is dried and added to the main portion.

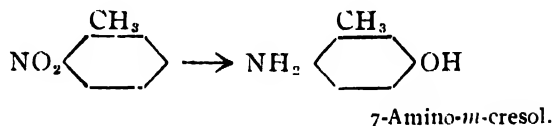
The product of reduction of *m*-nitroaniline and 2:4-dinitrophenol being, in each case, 2:4-diaminophenol, its mode of isolation is different from that of the mono-aminophenols. In these reductions therefore after the electrolysis, the acid solution is cooled and filtered to remove unreduced nitro compounds (in the cases of *m*-dinitrobenzene and 2:4-dinitrophenol) and the clear solution concentrated under reduced pressure in an atmosphere of hydrogen. As soon as solid begins to separate the concentration is stopped and the contents cooled and filtered on a glass sintered crucible, the solid being pressed to remove as much of the sulphuric acid as possible. The sulphate thus obtained is dissolved in a little boiling water, the filtered solution poured into 10 times its volume of absolute alcohol, cooled and kept in the frigidaire. The precipitated sulphate is filtered off and the alcohol recovered from the filtrate. The sulphate is finally dried over sulphuric acid in an evacuated desiccator and weighed. In order to determine the purity of the diaminophenol sulphate, the nearly insoluble oxalate is prepared from each sample of the sulphate and the yields of diaminophenol formed calculated, based on these values.

The precipitation of diaminophenol oxalate from the sulphate is conducted as follows:—5 g. of the sulphate are dissolved by warming in 15 c.c. of water, and a solution of 5 g. of potassium oxalate in 25 c.c. of hot water added, the temperature of the mixed solution being about 40°. White crystals of diaminophenol oxalate begin to separate almost immediately. They are filtered after cooling in the frigidaire, washed with a small quantity of cold water and dried in a vacuum desiccator.

The more important of the observations made and the results obtained during this investigation are given below.

1. *Nitrobenzene* (See Dey, Govindachari and Rajagopalan, *J. Sci. Ind. Res.*, 1946, **5A**, pp. 574-81).—In the small-scale experiments, conducted mostly in the nature of preliminary investigations, using 100 g. of nitrobenzene at a time, the most satisfactory results were obtained with copper or monel cathodes in the presence of mercury. Experiments were then conducted on a larger scale with the cathode combinations which proved satisfactory in the small-scale experiment and using 1,000 to 1,500 g. of nitrobenzene at copper or monel cathode and lead anode with a catholyte consisting of sulphuric acid of density 1.2 and containing 0.5 to 1.0% of mercury or cerium salt on the weight of nitrobenzene taken. The process is superior in simplicity of operation, high yield and purity of product and low upkeep charges, to the many other methods cited earlier in this paper, and would therefore be most suitable for adoption on a technical scale. Moreover, the nitrobenzene is reduced in a state of emulsion in dilute sulphuric acid containing acid only a little more than what is required for neutralisation of the product formed. The cathode and anode are of metals which are low in cost and of which plentiful supplies can be had. The corrosion of the electrodes is negligible. The cell voltage is reasonably low and the yield per kw.hr. is nearly 90 g., nearly double that obtained in Gattermann or modified Gattermann procedures. The *p*-aminophenol was of high purity, was almost colourless and melted sharply at 183°.

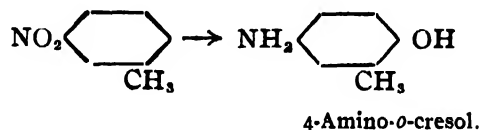
2. *o*-Nitrotoluene (Dey, Maller and Pai, *ibid.*, 1948, **7B** (8), 107-113).



The electro-reduction of *o*-nitrotoluene in acid emulsion can give rise mainly to two products, viz., *o*-toluidine and 4-amino-*m*-cresol. As a result of this investigation, the highest yield of the aminocresol (46% of theory) was obtained when an amalgamated monel cathode was employed in the presence of copper sulphate as catalyst (5-10 g.). The best acid concentration was 30% and so far as the extent of reduction is concerned, although perhaps not so far as the material yields go, lower concentrations serve equally well, e.g., 20%.

3. *m*-Nitrotoluene (Dey, Maller and Pai, *loc. cit.*, pp. 113-115).—*m*-Nitrotoluene was treated under the same conditions as those found best for the reduction of its *ortho*-isomer, viz., catholyte: 100 g. in 400 c.c. of 30% sulphuric acid; anolyte: 50 c.c. of 30% sulphuric acid; cathode: amalgamated monel; anode: lead; temperature:

70-75°; current density: 3.9 amps./sq.dm.; current strength: 20 amps./hr.; total current passed (theoretical): 80 amp.hrs.; 88.8% of the nitro compound were reduced, yielding 55.2% (by theory) of 4-amino-*o*-cresol and 15.9% (by theory) of *m*-toluidine.



4. *o*-Nitrochlorobenzene.—The best conditions worked out and results obtained so far in connection with the acid electrolysis of *o*-nitrochlorobenzene are given below:

Conditions:—Cathode: copper; catholyte: 100 g. of *o*-nitrochlorobenzene in 100 c. c. of xylene and 400 c.c. of 30% sulphuric acid; anode: lead; anolyte: 50 c.c. of 30% sulphuric acid; catalyst: 10 g. of copper sulphate; temperature: 50-55°; current strength: 20 amps./hr; current density: 5.99 amps./sq.dm.; total current passed: 84 amp. hrs. (theoretical).

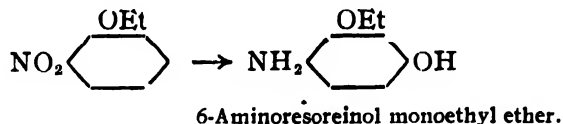
Results:—Current efficiency: 54%; *o*-chloroaniline: 24% of theory; *m*-chloro-*p*-aminophenol: 29.1% of theory.



5. *o*-Nitrophenetole.—The reduction of *o*-nitrophenetole to 6-aminoresorcinol-monoethyl ether (6-amino-3-hydroxy-1-ethoxybenzene, m.p. 170°) has been conducted under the following conditions: 100 g. of *o*-nitrophenetole (b.p. 187-189° at 20 to 22 mm.) in a catholyte of 400 c.c. of 30% sulphuric acid; anolyte: 50 c.c. of the same acid; catalyst: copper sulphate, 10 g.; cathode: monel; anode: lead; temperature: 80-85°; current strength: 20 amps./hr. and total current passed (theoretical): 64.2 amp. hrs.; current density: 3.9 amps./sq.dm.

Results:—Current efficiency: 75.3%; yield of 6-aminoresorcinol-monoethyl ether: 34.7%; yield of *o*-phenetidine: 19.4%

Note: 6-Aminoresorcinol-monoethyl ether has not been described in literature.



6. *m*-Dinitrobenzene (Dey and Udupa, *ibid.*, 1947, **6B**, 83-90).—The reduction of *m*-dinitrobenzene kept in a state of emulsion in dilute sulphuric acid was conducted systematically. As a result of this study the following points have come to light:

(1) At copper and monel cathodes, 2,4-diaminophenol can be obtained in nearly 35 to 45% yield by employing sulphuric acid of 40% strength, and using mercuric



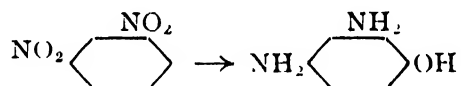
sulphate and ceric sulphate in combination as catalysts. Lower strengths of acid do not favour the formation of the diaminophenol, and the use of any strength higher than 50% not only does not improve the yields but also at the same time leads to corrosion of the cathodes and anodes.

(2) In order to obtain the best yield of the diaminophenol the ratio of depolariser to acid should be maintained at 1: 5.3.

(3) A current density of 7.69 amps./sq.dm. in the case of copper and 4.55 amps./sq.dm. in the case of monel seems to be the optimum when sulphuric acid of 40% strength is used.

(5) As regards the effect of addition agents, especially of mercuric and ceric sulphates, it was noticed that in the absence of the latter agents, the yield of diaminophenol was very low.

As a result of the above studies, a method has now been fully worked out for the preparation of 2:4-diaminophenol. It has been isolated as either the oxalate or sulphate in a maximum yield of 45%. For the purpose, *m*-dinitrobenzene kept in a state of emulsion by stirring with a solvent in a 40% sulphuric acid catholyte was reduced at a copper or monel cathode in the presence of addition agents like mercuric and ceric sulphates, at a temperature of 90°-95°. The formation of *m*-phenylenediamine in small amounts as a by-product was proved by the preparation and analysis of the dibenzoyl derivative from the mother-liquor left after the sparingly soluble diaminophenol oxalate had been precipitated.



7. *m*-Nitroaniline (Dey, Maller, Pai and Udupa, *ibid.*, 1948, **7B**, 53).—The reduction of *m*-nitroaniline in acid medium was conducted systematically on the same lines as in the cases of the reduction studies with *m*-dinitrobenzene. The following conclusions were drawn from the results obtained :

(1) The concentration of sulphuric acid which gives the best yield of 2:4-diaminophenol is 40%.

(2) A current density of 2.4 amps./sq.dm. in the case of monel, 2.0 amps./sq.dm. for copper and 3.85 amps./sq.dm. for nickel cathodes appears to be the optimum with sulphuric acid of 40% strength.

(3) For realising the best yields it is found essential to use about one-third more than the theoretical current necessary for the reduction.

(4) Increase of temperature betters the yield up to 80°, which is found to be the optimum.

(5) Copper sulphate, when copper is used as the cathode, mercuric sulphate for monel and nickel sulphate for nickel cathodes catalyses the reductions and high yields of diaminophenol sulphate are obtained (about 74% of theory).

(6) Monel, copper and nickel serve almost equally well as cathode materials.

(7) From the results of changing the concentration of depolariser, it appears that the ratio of one part by weight of *m*-nitroaniline to 10.5 parts by weight of the sulphuric acid content is the optimum for obtaining the maximum yield of diaminophenol, taking into consideration only the yield of the oxalate which is purer than the sulphate.

8. 2:4-Dinitrophenol (Löb, *Z. elektrochem.*, 1898, 4, 436).—The experimental details in connection with this reduction are exactly similar to those adopted for *m*-nitroaniline. A yield of 81% of the diaminophenol was obtained at a copper cathode without any addition agent in a 30% sulphuric acid catholyte, kept at 90°. Only the theoretical amount of current (17.5 amps. hrs.) was passed at 20 amps./hr. The best yields of the diaminophenol sulphate are obtained in small-scale experiments with 10 g. of dinitrophenol in 400 c.c. of 30% sulphuric acid. It may be mentioned here that the yields of diaminophenol sulphate decrease when catalysts like mercuric sulphate, copper sulphate, ceric sulphate and copper powder are used.

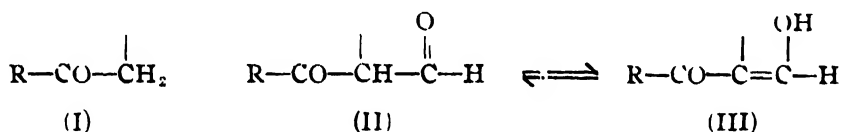
I commenced this memorial lecture with a recital of my personal reminiscences of Professor Prafulla Chandra Ray's life and I cannot perhaps do better than conclude it with the words of Sir Edward Thorpe which appeared in *Nature* of March, 6, 1919 and which seem to be peculiarly appropriate to-day : "Her (India's) elevation will not come in Sir Prafulla Chandra Ray's time. He will be spent in her service. But the memory of these services will survive".

# ENOL CONTENT OF 2-FORMYL KETONES. (HYDROXYMETHYLENE KETONES)

BY MISHRI MAI, BOKADIA AND S. S. DESHPANDE

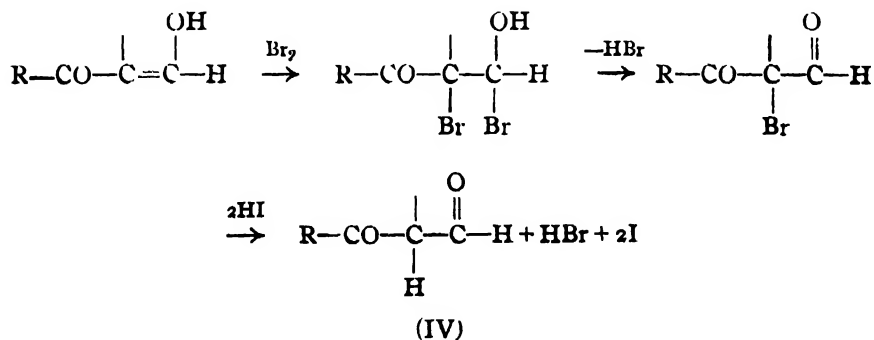
The enol content of some hydroxymethylene ketones has been determined

Formylation of ketone (I) gives the formyl derivative (II) which according to Claisen (*Ber.*, 1887, **40**, 2191) exists mostly in the enolic form (III) and is therefore known as hydroxymethylene ketone.



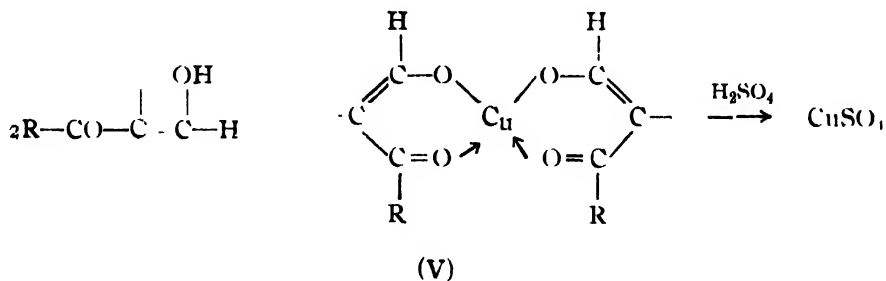
The actual determination of the enol content in the aldehyde-enol equilibrium mixture ( $\text{II} \rightleftharpoons \text{III}$ ) is the object of the present work.

We employed for this purpose the method of Meyer (*Be.*, 1911, **44**, 2718; 1912, **45**, 2843) of bromine titration which has been employed in the estimation of enol in keto-enol equilibrium mixture. Addition of bromine to the enol (III), followed by loss of hydrobromic acid, produces the bromo-aldehyde (IV). On adding potassium iodide the hydriodic acid formed reduces (IV) liberating two atoms of iodine per molecule of enol. The iodine is then estimated.



To check the correctness of the results obtained by this method we used another method due to Hibber (*Ber.*, 1921, **54**, 902) the principle of which is the estimation of copper in the chloroform-soluble chelate copper salt (V) which the enol forms on addition of

copper acetate. From this solution, on acidifying with sulphuric acid, copper sulphate separates which is estimated iodometrically. One half atom of copper corresponds to one molecule of enol.



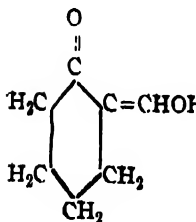
As will be seen from the experimental part, the two methods gave concordant results only in two cases. Generally, however, the results of enol estimation by Meyer's method are much higher than those obtained by Hibber's method. It appears that bromine used in the first method affects the equilibrium in aldehyde-enol system. A critical study of the disturbing effect of bromine in bromocarbonyl compounds in general will be the subject of the next communication.

#### E X P E R I M E N T A L

*Meyer's Method.*—The conditions laid down by the author were strictly adhered to. To the solution of hydroxymethylene ketone in absolute alcohol, kept at  $-10^\circ$ , was added alcoholic  $N/5$ -bromine in slight excess, the excess being removed by adding alcoholic 10% solution of  $\beta$ -naphthol until the pale yellow colour due to excess of bromine just disappeared. The whole operation was completed within 15 seconds and at  $-10^\circ$ . Potassium iodide was then added, the mixture was warmed and the liberated iodine titrated against  $N/10$ -sodium thiosulphate.

*Hibber's Method.*—The author's experimental conditions were followed. A weighed quantity of the hydroxymethylene ketone was dissolved in 30 c.c. of absolute alcohol and the solution was cooled to  $-10^\circ$ . To this was added a mixture, kept at  $-10^\circ$ , of absolute alcohol (12 c.c.), chloroform (8 c.c.) and aqueous copper acetate (10 c.c. containing 0.0015 g. copper per c.c.). The whole was well stirred and poured into a separating funnel containing 250 c.c. of water at  $0^\circ$ . The whole operation was finished within 15 seconds. The layer of chloroformic copper-enol solution separating was transferred to another separating funnel; the contents of the first funnel were once more extracted with chloroform, the chloroform extracts were mixed, washed with water and decomposed by dilute sulphuric acid. Copper in the aqueous layer of copper sulphate which separated was estimated iodometrically. The percentages of enols obtained by these two methods are shown in the following table.

TABLE I

Hydroxymethylene ketones.	Formula.	Percentage of enol by		Reference
		Meyer's method.	Hibber's method.	
1. Hydroxymethylene methyl ethyl ketone	$\text{Me}-\text{CO}-\underset{\text{  }}{\text{C}}-\text{Me}$ $\text{CHOH}$	96.1	64.1	Joshi, Kaushal and Deshapande ( <i>this Journal</i> , 1941, 18, 479).
2. Hydroxymethylene diethyl ketone	$\text{Et}-\text{CO}-\underset{\text{  }}{\text{C}}-\text{Me}$ $\text{CHOH}$	57.0	35.5	Claisen and Meyerowitz ( <i>Ber.</i> , 1889, 22, 3275).
3. Hydroxymethylene cyclohexanone		72.5	74.5	Wallach and Steindorff ( <i>Annalen</i> , 1903, 320, 117).
4. Hydromethylene desoxybenzoin	$\text{Ph}-\text{CO}-\underset{\text{  }}{\text{C}}-\text{Ph}$ $\text{CHOH}$	90.2	89.7	Wislicenus and Ruthing ( <i>Annalen</i> , 1911, 379, 238)
5. Bromohydroxymethylene acetophenone	$\text{Ph}-\text{CO}-\underset{\text{  }}{\text{C}}-\text{Br}$ $\text{CHOH}$	68.0	34.0	Agarwal, Gupta and Deshapande ( <i>this Journal</i> , 1949, 26, 55).

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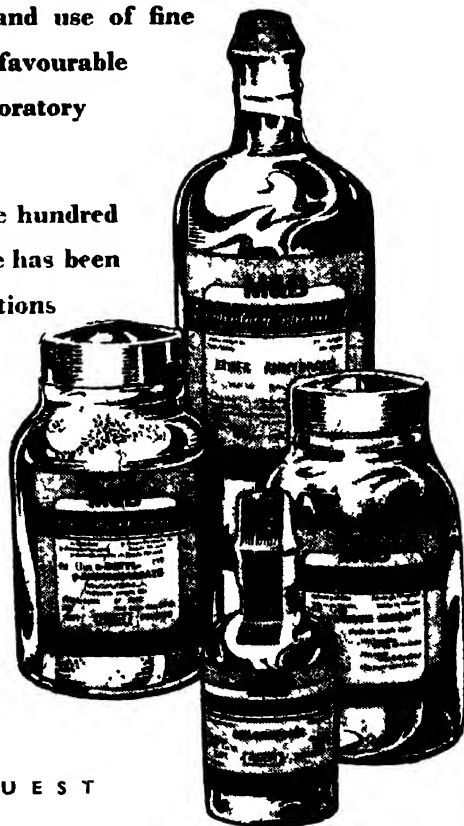
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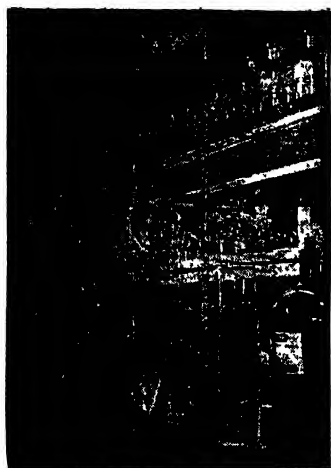
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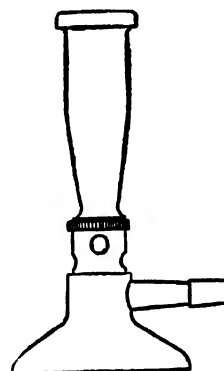
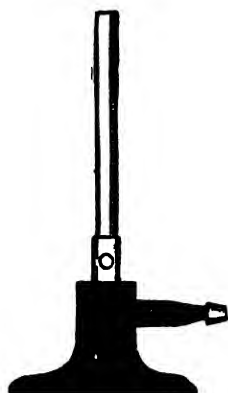
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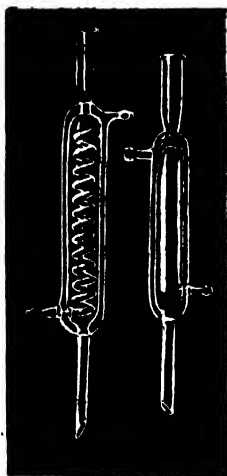


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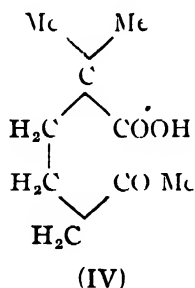
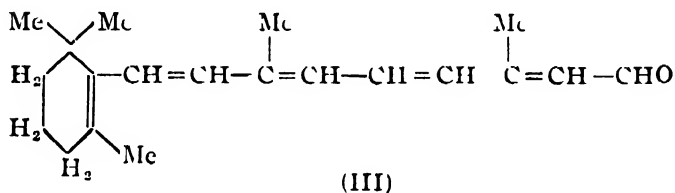
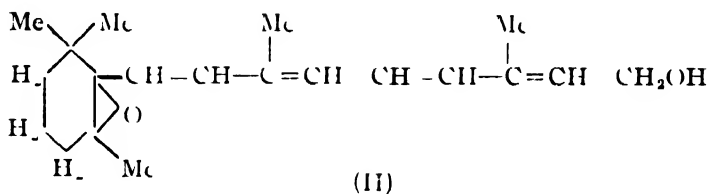
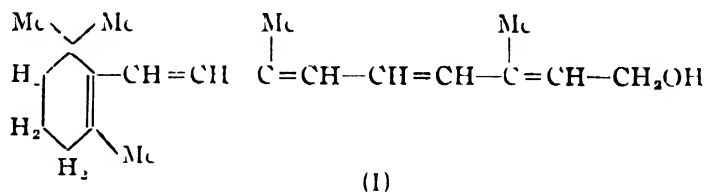
## STUDIES ON VITAMIN-A IN SOLUTION. PART II. MODE OF ACTION OF THE ANTIOXIDANT

BY U. P. BASU AND SUKHAMOY BHATTACHARYA

An attempt has been made to explore the mode of action of a hydroxy-phenolic antioxidant in retarding the onset of oxidation in vitamin-A molecule

Vitamin-A (I) is an unsaturated alcohol and in pure crystalline form it has been found to melt at 63-64°. But in its natural form it is present both in the free alcoholic and in an ester (palmitate) form (Tischer, *J. Biol. Chem.*, 1938, **125**, 475). Recently Robeson and Baxter (*J. Amer. Chem. Soc.*, 1947, **69**, 136) have again shown that certain shark-liver oils contain up to 35% of the total vitamin in a form which is a *trans-cis* isomer of the normal vitamin (*trans-trans* variety). The two isomers differ in the spacial configuration about the double bond nearest the hydroxyl group, the *trans-cis* being more resistant than the normal one. Similarly the observations of Baxter and Robeson (*J. Amer. Chem. Soc.*, 1942, **64**, 2407) and that of Basu and Sen Gupta (*ibid.*, 1948, **70**, 413) tend to show that whether in natural form or in the artificial fortified food, the vitamin ester is more resistant than the free alcohol to atmospheric oxidation. This oxidative change may be considerably controlled by incorporation of a suitable antioxidant (cf. Whipple, *Oil & Soap*, 1936, **13**, 231; Lowen, Anderson and Harrison, *Ind. Eng. Chem.*, 1937, **29**, 151; Basu, *Ann. Biochem. Exp. Med.*, 1941, **1**, 105). As the vitamin is usually present in some fat or oil, this oxidation is believed to be due to an onset of oxidation in the unsaturated molecule of the latter substance. An earlier observation of Basu (*loc. cit.*) indicates that the deterioration of the vitamin-A cannot be accounted for by the above change only. Vitamin-A itself is an unsaturated body with five unsaturated bonds, four in the aliphatic side chain and one in the ionone ring. It is not entirely clear whether the relation of unsaturation to physiological activity resides solely in the  $\beta$ -ionone ring or whether some unsaturation in the side chain is also important. The unsaturated bond in the  $\beta$ -ionone ring is oxidisable to an epoxide (II) under the influence of perphthalic acid (Karrer and Jucker, *Helv. Chim. Acta*, 1945, **28**, 717; 1947, **30**, 559) and the alcoholic group also undergoes oxidation to vitamin-A aldehyde (III) when heated with aluminium isopropoxide in the presence of acetaldehyde (Hawkin and Hunter, *J. Chem. Soc.*, 1944, 411). Hunter and Krakenberger (*ibid.*, 1947, 1) have recently shown that  $\beta$ -carotene, the precursor of vitamin-A, undergoes oxidation in solution by oxygen to  $\beta$ -carotene epoxide (of the type II) which subsequently undergoes fission to give rise to an open-chain ketone. Vitamin-A also under the action of ozone yields geronic acid (IV). Whatever may be the product or products of oxidation, it is a fact that the unsaturated bonds readily absorb oxygen in solution and are markedly pro-oxygenic in nature. Highly oxidised vitamin-A has no biological activity too, and as such if the inherent cause and mode of oxidation be known, it would be much easier to control the deterioration of the vitamin during isolation (cf. Rao, *Ind. J. Med. Res.*,

1945, **33**, 63) as well as in any pharmaceutical or food preparation (cf. Basu, *Ind. Pharm.*, 1943, **3**, 47).



At the very outset it may be noted that the autoxidation of fat is now believed (cf. Farmer, *Trans. Faraday Soc.*, 1946, **42**, 228 ; Bollard and Gee, *ibid* , 1946, **42**, 236) to be due to the formation of a free radical by detachment of an  $\alpha$ -methylene hydrogen ion. The function of an antioxidant of a hydroxy-phenolic type would be to prevent the formation of such a radical and of hydro-peroxides. The antioxidant interrupts the chain of reactions leading to oxidation through direct diversion of the original activated fat molecules. The observations of Calkins (*J. Amer. Chem. Soc.*, 1947, **69**, 384) further show that an acid inhibitor in such cases by donating protons would help in regenerating the further hydroxy antioxidant and thereby insure its continuous supply to the system. If vitamin-A, an unsaturated body, behaves in a similar way, it is natural to expect that a saturated diluent like liquid paraffin will play no part in the course of oxidation of the vitamin molecule. This has been actually observed in part I of this series (this *Journal*, 1949, **26**, 419). The incorporation of a hydroxy-phenolic

antioxidant in this case also by preventing the formation of hydro-peroxide helps in protecting the vitamin from deterioration. As the ester or glyceride has been further found to inhibit the onset of oxidation, it may be argued that the ester by incipient formation of an acid-like body is either forming a complex with the vitamin molecule, or, is helping the continuity of hydroxy antioxidant in the system. In order to find out the role of the antioxidant in preventing the deterioration of vitamin-A molecule further work has been continued and the results of these observations have been recorded in the body of this paper.

#### EXPERIMENTAL

*Nature of the Antioxidant.*—Hydroquinone containing two hydroxyl groups is a good antioxidant for vitaminised oil (Basu, *loc. cit.*). In the course of this investigation monomethyl ether of hydroquinone (m.p. 54-56°), dimethyl ether of hydroquinone (m.p. 54-55°) and propyl gallate (m.p. 146-48°) were prepared. They are soluble in oils and esters. In case of propyl gallate, which is not readily soluble in liquid paraffin, the antioxidant was first dissolved in a few drops of peroxide-free ether and the solution was mixed with liquid paraffin. Each of mono and dimethyl ether of hydroquinone was dissolved in 25 c.c. of ethyl oleate containing 740 I.U. of vitamin-A per g. in an amber coloured resistant bottle fitted with perforated corks for aeration under negative pressure. The concentration of both the antioxidants in the preparation was 0.05%. Samples were withdrawn at intervals and the vitamin-A contents were estimated by the procedure as laid down in the previous paper (*loc. cit.*). The results are shown in Table I.

*Role of Oleic Acid in Liquid Paraffin System.*—The characteristic behaviour of esters in vitamin-A preparations indicates that a simple acid molecule may also play a similar role in protecting vitamin-A from oxidation. With this idea in view three preparations, each containing 1100 I.U. of vitamin-A per g., were made in (i) simple liquid paraffin (25 c.c.) ; (ii) in liquid paraffin (25 c.c.) containing 0.05% propyl gallate, and (iii) in liquid paraffin containing 0.05% propyl gallate and 0.14% oleic acid. Dry and purified air was passed and samples were withdrawn and assayed for vitamin-A in the customary way. Results are recorded in Table II.

*Influence of Water in Liquid Paraffin System.*—Preparation of vitamin-A containing 1100 I.U. per g. was made with liquid paraffin and water (liquid paraffin : water = 1:2) was added to it in presence of 0.05% propyl gallate. The system was aerated and as it was difficult to withdraw representative sample of the mixture, the whole after 191 hours' aeration was extracted with peroxide-free ether (thrice with 50 c.c. portions). The volume was reduced to about 50 c.c. by evaporation of ether and again the volume was made up to 100 c.c. with ether in a volumetric flask. An aliquot part of this solution was taken for vitamin-A assay. The results are shown in the last two columns of Table II.

*Peroxide Formation in Vitamin-A.*—Two preparations containing 1100 I.U. of vitamin-A per g. were made from vitamin-A concentrate in liquid paraffin, one being without the addition of any antioxidant and the other with 0.05% propyl gallate. Both were aerated and the peroxide formed was determined at intervals according to Basu and Mazumder (*Leprosy in India*, 1939, 11, 53). The peroxide value has been

expressed as the number of c.c. of 0.002*N*-sodium thiosulphate per g. of the preparation (vide Table III).

*Deterioration in Vitamin-A Acetate.*—Two gelatin capsules of vitamin-A acetate each containing 2500 U.S.P. units of vitamin-A were taken in 10 c.c. of ethyl oleate of the specification described in the previous paper (*loc. cit.*). The tips of the capsules were cut with fine scissors and the contents were well mixed and the vitamin-A potency of the solution was on analysis found to contain 570 I.U. per g. (this is equivalent to 496 I.U. per ml., theoretically it should have been 500 I.U. per c.c.). A similar preparation was made with ethyl stearate of the specification described in the previous paper and on assay was found to contain 513 I.U. of vitamin-A per g.

This showed that vitamin-A acetate did not undergo any initial loss of potency when dissolved in fatty esters unlike the free vitamin-A alcohol molecule. Both the preparations were then subjected to aeration (4 c.c. per second) with purified and dried air. Samples were withdrawn at intervals and assayed for vitamin-A content. The results are recorded in Table IV.

TABLE I  
*Ethyl oleate.*

Duration of aeration.	Without antioxidant.		With 0.05% dimethyl hydroquinone		With 0.05% monomethyl hydroquinone	
	Vitamin-A (I. U./g.)	% Loss of vitamin-A.	Vitamin-A (I. U./g.)	% Loss of vitamin A	Vitamin A (I. U./g.)	% Loss of vitamin-A.
0 hr.	740	0	740	0	740	0
52	300	59.5	—	—	—	—
59	—	—	282	61.9	—	19.6
66	—	—	—	—	595	—
94	196	73.5	—	—	—	—
100	—	—	193	74.0	535	27.7
149	190	74.3	—	—	—	—
160	—	—	—	—	513	30.7
177	—	—	184	75.1	—	—

TABLE II  
*Liquid paraffin.*

Duration of aeration.	Without antioxidant.		With 0.05% propyl gallate		With 0.05% propyl gallate + 0.14% oleic acid.		With 0.05% propyl gallate + water.	
	Vitamin-A (I. U./g.)	% Loss of vitamin-A	Vitamin-A (I. U./g.)	% Loss of vitamin-A.	Vitamin-A (I. U./g.)	% loss of vitamin-A.	Vitamin-A (I. U./g.)	% loss of vitamin-A.
0 hr.	1100	0	1100	0	1100	0	1100	0
87	512	53.5	658	40.2	773	29.7	—	—
142	305	72.3	620	43.7	755	31.4	—	—
191	222	79.8	610	44.6	750	31.8	800	27.3

TABLE III

*Peroxide formation of vitamin-A alcohol in liquid paraffin.*

Conc. of vitamin-A = 1100 I.U./g.

Duration of aeration.	Without antioxidant. Peroxide value (ml. of 0.002N-thio per g.)	With 0.05% propyl gallate. Peroxide value (ml. of 0.002N-thio per g.)
0 hr	Nil	Nil
134	1.91	-
180	3.10	0.75

TABLE IV

*Vitamin-A acetate system without antioxidant.*

Duration of aeration.	Vitamin-A acetate in ethyl oleate		Vitamin-A acetate in ethyl stearate.	
	Vitamin-A (I. U./g.)	% Loss of vitamin-A.	Vitamin-A (I. U./g.)	% Loss of vitamin-A.
0 hr.	570	0	513	0
80	12	24.7	416	18.9
135	423	25.8	—	—
142	—	—	390	24.0
184	—	—	340	33.7
190	410	28.1	—	—

TABLE V

*Loss of vitamin-A in various systems.*

Vitamin-A alcohol

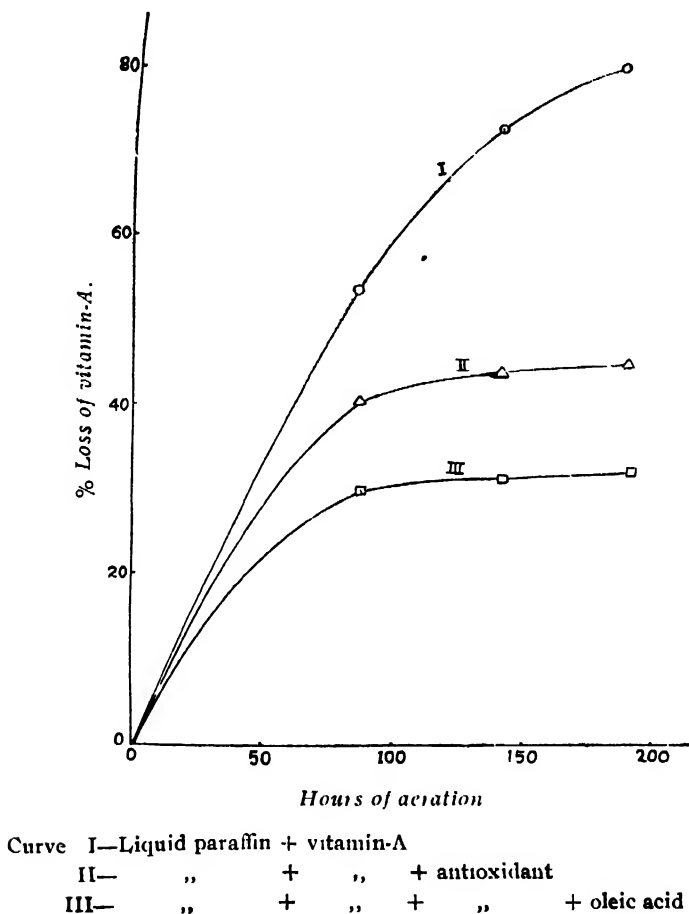
Systems.	Duration of aeration.	Without antioxidant.	Duration of aeration.	With antioxidant.
Arachis oil	149 hr.	76.2%	177 hr.	31.3%
Ethyl oleate	149	74.3	160	30.7
Ethyl stearate	156	46.9	184	31.3
Liquid paraffin	191	79.8	191	46.6
Liquid paraffin + ethyl oleate	192	82.1	192	35.7
Liquid paraffin + ethyl stearate	177	60.9	185	24.8
Liquid paraffin + glyceryl monolaurate.	170	68.7	177	13.6

## DISCUSSION

It is apparent from the results so far obtained that the cause of deterioration of vitamin-A is due to a sort of oxidation in the molecule with the formation of a peroxide-like body (type VI). The formation of such peroxide body has been lowered by about 75% on addition of an antioxidant in liquid paraffin *cum* vitamin-A system (vide Table III). From Table I it will be noticed that the loss of vitamin in ethyl oleate, when adjuvated with 0.05% dimethylhydroquinone, is 75.1% after 177 hours' aeration and this compares well with the system containing no antioxidant, whereas monomethylhydroquinone (0.05%) protects 69.7% of the vitamin-A potency. From this and also from the protective action of propyl gallate (cf. part I, *loc. cit.*) it appears that for exerting antioxygenic function the compound must contain one or more free phenolic hydroxyl groups.

The function of the hydroxy antioxidant most probably lies in the formation of some complex of the type (VII) and thereby preventing the vitamin-A alcohol molecule from absorbing oxygen at the unsaturated linkage present in the  $\beta$ -ionone ring (the more susceptible bond of the molecule) to form a peroxide of the nature (VI). This is some-

FIG. 1

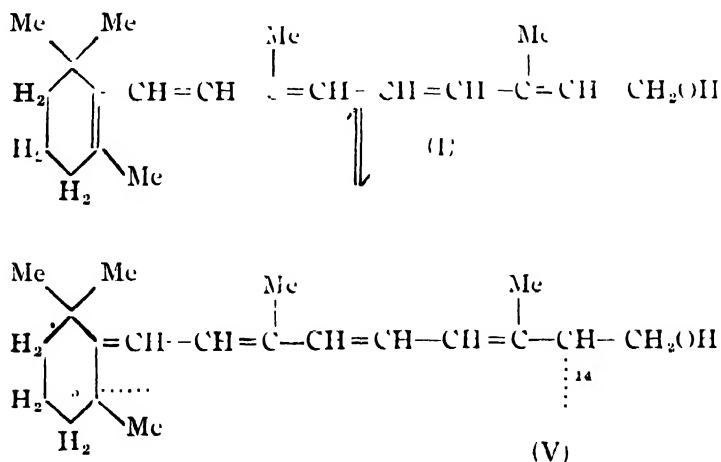


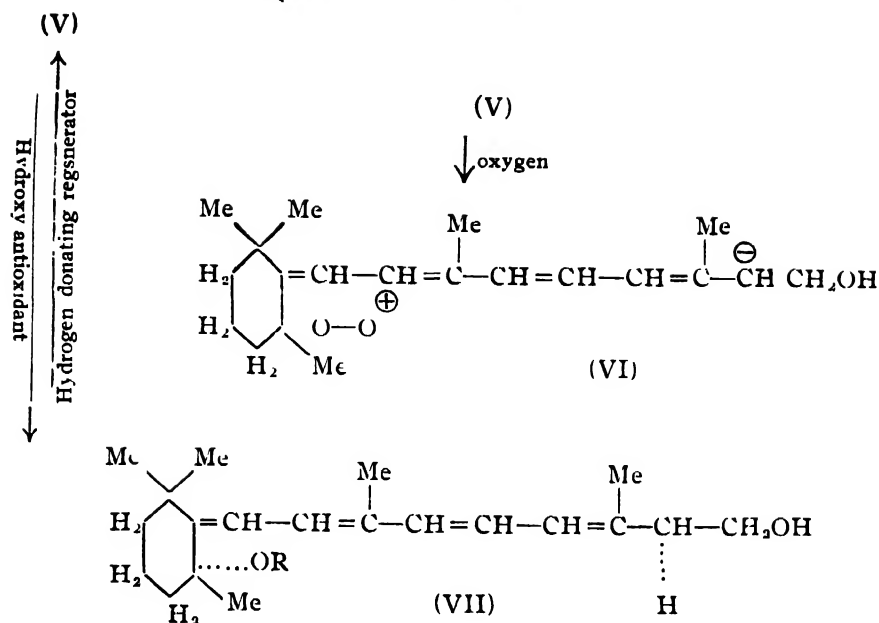
what substantiated by the fact that the loss of vitamin-A potency comes down to 44.6% from 79.8% after 191 hours' aeration when the vitamin in saturated diluent (liquid paraffin) contains an antioxidant (cf. Table II and the curves I and II, Fig 1).

But during the formation of the complex of the type (VII), where the antioxidant becomes bound with the vitamin-A molecule, there would be gradual shortage of the antioxidant till it is exhausted and would thereby cease to exert its antioxygenic function any more. In order to maintain its function the antioxidant needs regeneration from the complex by some hydrogen donating substance when the vitamin-A also will be free again to exert its characteristic reaction. The continuity of the supply of antioxidant to the system and the maintenance of vitamin-A will then remain practically unaffected. Such regeneration of the antioxidant may be seen from Table II and also from the curves II and III of Fig. 1, where trace of oleic acid as well as water, both of which have ionisable hydrogen atom individually, helps the antioxidant to maintain the vitamin-A potency in liquid paraffin to a higher degree than the system containing no such hydrogen donor.

It is interesting to note that the loss of vitamin-A in a liquid paraffin system containing antioxidant and some hydrogen donating substance compares well with the systems containing esters or glycerides with antioxidant (vide Tables I, II and V).

The above postulate on the mode of function of the antioxidant and its regeneration may be extended to the case of esters or glycerides. In presence of an antioxidant an ester or glyceride, natural or synthetic, seems to play a part like that of oleic acid when added to a solution of vitamin-A in liquid paraffin. From the data in Table V it will be evident that a similar inhibition is obtained when the vitamin is dissolved in a pure ester or glyceride with an antioxidant. This inhibiting action may be attributed to the incipient formation of free acid in the system which in turn regenerates the antioxidant from the complex of the type (VII). The mode of reaction of the antioxidant with vitamin-A molecule may be represented as follows :





The vitamin-A alcohol (type I) containing conjugated double bonded systems may undergo a prototropic change and in the return of the proton the 5 and 14 carbon atoms of the conjugated system may become activated (cf. type V) and form a peroxide of the type (VI). In presence of hydroxy-phenolic antioxidant it may, however, form a complex (type VII). The latter under the influence of a hydrogen donating substance would undergo fission to regenerate the antioxidant and the vitamin to play their respective role.

The replacement of the mobile hydrogen atom of the vitamin-A alcohol by esterification would tend to lower its prototropic change and consequently its susceptibility to receive an electronic charge. This would prevent the formation of peroxide-like body of the type (VI). Most probably it is for this reason that preparations made with vitamin-A acetate in ethyl stearate or even with ethyl oleate without the presence of antioxidant retain the vitamin-A potency on aeration to a degree comparable to preparations made with vitamin-A in alcohol in presence of antioxidant (vide Tables IV and V).

It has been noticed that the vitamin-A alcohol, when dissolved in glycerides or esters, loses a portion of its potency, whereas in the case of vitamin A acetate no such initial loss has been experienced. In liquid paraffin medium too, no initial loss is noticed with vitamin-A alcohol. It appears that the antioxidant is not functioning to react with the peroxide already formed in the system but exerts its influence to prevent the further formation of the peroxide. The reported stability of Neo-vitamin-A may also be studied from this angle. Further investigations are being continued.

#### CONCLUSION

The antioxidant must contain a phenolic 'OH' and its antioxygenic function is enhanced by suitable hydrogen donor. The vitamin-A alcohol is susceptible to the easy formation of a peroxide which is retarded by the presence of an antioxidant. The vitamin-A ester, however, is less susceptible to oxidation.



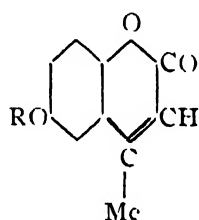
# BROMINATION OF COUMARINS. PART II. BROMINATION OF 6-HYDROXY-4-METHYLCOUMARIN AND ITS METHYL ETHER

By VIJAY JAYAWANT DALVI AND SURESH SETHNA

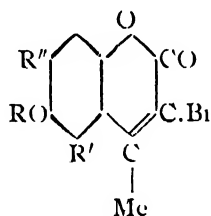
6-Hydroxy-4-methylcoumarin and its methyl ether have been brominated and mono, di- and tribromo derivatives obtained.

In continuation of the work described in part I (*this Journal*, 1949, 26, 359) the bromination of 6-hydroxy-4-methylcoumarin and its methyl ether has been studied.

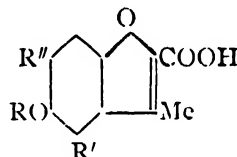
Borsche (*Ber.*, 1907, 40, 2732) carried out the bromination of 6-hydroxy-4-methylcoumarin with two molecules of bromine and arbitrarily assigned the constitution of 6-hydroxy-5:7-dibromo-4-methylcoumarin to the product obtained. In the bromination of 7-hydroxy-4-methylcoumarin (part I) it has been found that the first bromine atom enters the 3-position and the subsequent bromine atoms enter the benzene ring. It was therefore of interest to study the bromination of 6-hydroxy-4-methylcoumarin and its methyl ether systematically.



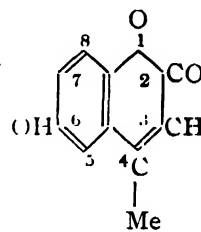
(I)



(II)



(III)



(IV)

6-Hydroxy-4-methylcoumarin (I, R=H) on bromination with one molecule of bromine did not give a pure product. Its methyl ether (I, R=Me), however, under the same conditions of bromination gave a bromo compound to which the structure of 6-methoxy-3-bromo-4-methylcoumarin (II, R=Me; R'=R''=H) was assigned, as it gave a coumarilic acid derivative (III, R=Me; R'=R''=H) on treatment with alkali. This methoxy bromocoumarin on demethylation with anhydrous aluminium chloride gave 6-hydroxy-3-bromo-4-methylcoumarin (II, R=R'=R''=H).

6-Hydroxy-4-methylcoumarin on bromination with two molecules of bromine in acetic acid at the temperature of the water-bath gave a dibromo compound (A, m.p. 276-80°). However, when the bromination was carried out in acetic acid solution with two molecules of bromine in presence of sodium acetate, as done by Borsche (*loc. cit.*), another dibromo compound (B, m.p. 201-203°), probably identical with Borsche's derivative (m.p. 202-203°), was obtained. Borsche has arbitrarily assigned to it the structure of 6-hydroxy-5:7-dibromo-4-methylcoumarin. Both the compounds (A) and (B) were methylated. Both the dibromocoumarins on hydrolysis gave coumarilic acid derivatives, thus indicating that one of the bromine atoms in both was in 3-position. The other

bromine atom must therefore be either in the 5- or in the 7-position. The structure assigned by Borsche to the dibromocoumarin is therefore incorrect. The structures of 6-hydroxy-3:7-dibromo-4-methylcoumarin (II,  $R=R'=H$ ;  $R''=Br$ ) and 6-hydroxy-3:5-dibromo-4-methylcoumarin (II,  $R=R''=H$ ;  $R'=Br$ ) are provisionally assigned on stereochemical grounds to (A) and (B) respectively.

If we assume that in the coumarin ring system the double bond is fixed between the benzene ring and the  $\alpha$ -pyrone ring (cf. Mills and Nixon, *J. Chem. Soc.*, 1930, 2510; Rangaswami and Seshadri, *Proc. Ind. Acad. Sci.*, 1941, **14A**, 547; Thakor and Shah, *J. Univ. Bombay*, 1947, XVI, Part 3, p. 38) the 5-position ought to be more reactive than the 7-position, because there is a double bond between the fifth and the sixth carbon atoms and the sixth carbon atom carries the hydroxyl group (Formula IV). However, owing to the steric hindrance of the hydroxyl group in 6-position and the methyl group in 4-position, the bromine atom is not likely to enter the 5-position with ease. In the case of the bromination of 6-methoxy-4-methylcoumarin the steric hindrance will be more marked due to the methoxy group and therefore it is presumed that the only dibromo product obtained on bromination may be 6-methoxy-3:7-dibromo-4-methylcoumarin (II,  $R=Me$ ;  $R'=H$ ,  $R''=Br$ ). This compound is identical with the methyl ether of (A); therefore A is probably 6-hydroxy-3:7-dibromo-4-methylcoumarin. It follows therefore that (B) must be 6-hydroxy-3:5-dibromo-4-methylcoumarin.

Both (A) and (B) on further bromination gave the same 3:5:7-tribromo derivative (II,  $R=H$ ,  $R'=R''=Br$ ) which was also obtained on bromination of 6-hydroxy-4-methylcoumarin with excess of bromine. Attempts to prepare the tribromo derivative of 6-methoxy-4-methylcoumarin did not succeed, only the dibromo compound was obtained.

#### EXPERIMENTAL

6-Hydroxy-4-methylcoumarin was prepared according to Borsche (*loc. cit.*) and methylated with dimethyl sulphate and alkali (Desai and Mavani, *Proc. Ind. Acad. Sci.*, 1942, **15A**, 11).

*6-Methoxy-3-bromo-4-methylcoumarin*.—The coumarin (I,  $R=Me$ ; 1.9 g.) was dissolved in acetic acid (10 c.c.) by heating, and bromine (1.6 g, 1 mol.) in acetic acid (16 c.c.) added to the hot solution. The reaction mixture was allowed to stand for 4 hours and then diluted with water. The separated solid was crystallised from dilute alcohol in faint yellow glistening needles, m.p. 125–27°, yield 1.5 g. (Found: Br, 29.9.  $C_{11}H_9O_3Br$  requires Br, 29.7 per cent).

*6-Hydroxy-3-bromo-4-methylcoumarin*.—6-Methoxy-3-bromo-4-methylcoumarin (1 g.) was intimately mixed with powdered anhydrous aluminium chloride (4 g.) and the mixture was heated in an oil-bath at 150°–160° for 3 hours. It was then cooled and treated with ice and concentrated hydrochloric acid and the solid obtained was crystallised from acetic acid in yellow needles, m.p. 258–60°, yield 0.6 g. (Found: Br, 31.2.  $C_{10}H_7O_3Br$  requires Br, 31.4 per cent). It forms orange-yellow alkali salts which are sparingly soluble in water.

**5-Methoxy-3-methylcoumarilic Acid.**—The bromocoumarin (II,  $R = \text{Me}$ ,  $R' = R'' = \text{H}$ ) (1 g.) was refluxed with potassium hydroxide solution (1 N, 20 c.c.) for 3 hours. It was acidified and the precipitated solid was crystallised from dilute acetic acid in small white plates, m.p.  $208^\circ$  (decomp.), yield 0.6 g. (Found: C, 63.8; H, 4.7.  $\text{C}_{11}\text{H}_{10}\text{O}_4$  requires C, 64.1; H, 4.8 per cent). It gives a violet coloration on warming with concentrated sulphuric acid.

**6-Hydroxy-3: 7 (or 5)-dibromo-4-methylcoumarin (A).**—The coumarin (I,  $R = \text{H}$ ) (1.76 g) was dissolved in acetic acid (15 c.c.) by heating and bromine (3.2 g., 2 mols.) in acetic acid (32 c.c.) added. The reaction mixture was heated on a boiling water-bath for 2 hours. The product which separated out was crystallised from acetic acid in small yellow plates, m. p.  $276-80^\circ$ , yield 1.2 g. (Found: Br, 47.6.  $\text{C}_{10}\text{H}_6\text{O}_3\text{Br}_2$  requires Br, 47.9 per cent).

The methyl ether of the above bromocoumarin was prepared by refluxing it with methyl iodide in acetone solution in presence of anhydrous potassium carbonate, m. p.  $205-207^\circ$ . (Found: Br, 45.9.  $\text{C}_{11}\text{H}_8\text{O}_3\text{Br}_2$  requires Br, 46.0 per cent). This was found to be identical with 6-methoxy-3: 7 (or 5)-dibromo-4-methylcoumarin (described below) prepared by the direct bromination of 6-methoxy-4-methylcoumarin.

**6-Hydroxy-3: 5 (or 7)-dibromo-4-methylcoumarin (B).**—The coumarin (I,  $R = \text{H}$ ) (1.76 g) and crystalline sodium acetate (3.5 g.) were dissolved in acetic acid (30 c.c.) by heating and bromine (3.2 g., 2 mols.) in acetic acid (32 c.c.) added gradually with shaking to the hot solution. The product which separated out on cooling was crystallised from dilute alcohol in silky white needles, m. p.  $201-203^\circ$ , yield 1.5 g. (Found: Br, 47.8.  $\text{C}_{10}\text{H}_6\text{O}_3\text{Br}_2$  requires Br, 47.9 per cent). It forms orange-yellow alkali salts which are sparingly soluble in water.

The methyl ether of the above bromocoumarin was prepared by refluxing a solution of the bromocoumarin in acetone with methyl iodide and anhydrous potassium carbonate for 20 hours, m. p.  $212-14^\circ$ . (Found: Br, 45.6.  $\text{C}_{11}\text{H}_8\text{O}_3\text{Br}_2$  requires Br, 46.0 per cent).

**6-Methoxy-3: 7 (or 5)-dibromo-4-methylcoumarin.**—The coumarin (I,  $R = \text{Me}$ ; 2 g.) was treated with liquid bromine (5 c.c., excess) and the mixture was allowed to stand for 48 hours. The residual solid was treated with sodium bisulphite solution to remove the excess of bromine. The product obtained was crystallised from acetic acid in silky white needles, m. p.  $205-207^\circ$ , yield 2.5 g. Mixed melting point with the methyl ether of the dibromocoumarin (A) was not lowered. Mixed melting point with the methyl ether of the dibromocoumarin (B) was lowered to  $182^\circ$ . The same dibromo product was obtained when the bromination was carried out with excess of bromine in presence of sodium acetate.

**5-Methoxy-6 (or 4)-bromo-3-methylcoumarilic Acid.**—6-Methoxy-3: 7 or 5-dibromo-4-methylcoumarin (1 g.) was refluxed with potassium hydroxide solution (1 N, 20 c. c.) for 3 hours. The solid separating on acidification was crystallised from acetic acid in white needles; m. p.  $274-76^\circ$  (decomp.), yield 0.6 g. (Found: Br, 28.2.  $\text{C}_{11}\text{H}_8\text{O}_4\text{Br}$  requires Br, 28.1 per cent). It gives a violet coloration when warmed with concentrated sulphuric acid.

**5-Hydroxy-4 (or 6)-bromo-3-methylcoumarilic Acid.**—The dibromocoumarin (B, 1 g.) was refluxed with sodium carbonate solution (5%, 20 c.c.) for 3 hours. The solid obtained on acidification was crystallised from dilute alcohol (charcoal) in brownish yellow shining needles, m. p.  $238-40^{\circ}$  (decomp.). (Found: Br, 29.5.  $C_{10}H_7O_4Br$  requires Br, 29.5 per cent).

**6-Hydroxy-3,5:7-tribromo-4-methylcoumarin.**—The coumarin (I, R=H) (2 g.) was treated with liquid bromine (5 c.c. excess) and the reaction mixture was kept for 48 hours. The residual solid was treated with sodium bisulphite solution to remove the excess of bromine and crystallised from acetic acid in short colorless needles, m. p.  $196-98^{\circ}$ , yield 2.8 g. (Found: Br, 58.1.  $C_{10}H_5O_3Br_3$  requires Br, 58.1 per cent). It forms orange-yellow alkali salts which are sparingly soluble in water.

The *methyl ether* of the above compound was prepared by refluxing it with methyl iodide in acetone solution in presence of anhydrous potassium carbonate. It was crystallised from acetic acid in small, yellow needles, m. p.  $174-76^{\circ}$ . (Found: Br, 56.5.  $C_{11}H_7O_3Br_3$  requires Br, 56.2 per cent).

**5-Hydroxy-4:6-dibromo-3-methylcoumarilic Acid.**—The bromocoumarin (II, R=II; R'=R''=Br) (1 g.) was refluxed with sodium carbonate solution (5%, 20 c.c.) for 3 hours. The solid separating on acidification was crystallised from dilute alcohol (charcoal) in small brownish plates, m. p.  $180^{\circ}$  (decomp.), yield 0.4 g. (Found: Br, 45.4.  $C_{10}H_5O_4Br_2$  requires Br, 45.7 per cent).

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## ELECTRODEPOSITION OF BRONZE FROM A CYANIDE BATH

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Electrodeposition of bronze from a bath containing copper cyanide, sodium stannate, cyanide and hydroxide of sodium was studied with respect to electrolyte concentration, current density, duration of electrolysis, temperature and addition agents. The optimum conditions for a satisfactory deposit on copper with respect to these factors are as follows :

The electrolyte concentration is such that the ratio of copper to tin is 1:3. The optimum C. D. is 0.76 amp/dm<sup>2</sup>. Cathode efficiency at the optimum C. D. is 62.5 %. Optimum duration of electrolysis is 20 minutes. Temperature of 60° is found to be the most suitable. Influence of addition agents like glycerol and sodium chloride is not well marked, though use of H<sub>2</sub>O<sub>2</sub> improves the deposit.

The bright silvery coating of bronze is superior to that of nickel or tin for protecting iron, steel and other metals, as it is less susceptible to atmospheric corrosion. The electroplated alloy is surpassed only by freshly plated silver in reflectivity and it is highly resistant to abrasion. The alloy can be soldered as easily as tin. These and the like are some of the remarkable properties of the alloy which attracted the attention of the electroplater. The work of Baier and Macnaughtan (*J. Electrodep. Tech. Soc.*, 1936, **11**, 14) and of Bechard (*Metal Progr.*, 1936, **29**, No. 3, 43, 94; *Chem. Zentr.*, 1936, **II**, 2217) has shown that Cu-Sn alloy of different compositions can be deposited in a satisfactory and adhesive form from an alkaline solution of Na<sub>2</sub>Cu(CN)<sub>3</sub> and Na<sub>2</sub>SnO<sub>3</sub> at 65°, using either carbon or bronze anode. Bechard (*Compt. rend.*, 1935, **200**, 1737) has also studied the electrodeposition of the alloy from solutions of stannic-ammonium and copper-ammonium oxalates. The information available in the literature on the quantitative data for bronze deposition is very meagre. In the present investigation an attempt has therefore been made to study the deposition of the alloy quantitatively in regard to the influence of a number of factors.

### EXPERIMENTAL

The electrolysis was carried out in a round glass trough, about 3' deep, and having a capacity of about 250 c.c. It was kept immersed in a thermostat and maintained at the desired temperature. The temperature of the bath solution was controlled within  $\pm 2^\circ$ . The anode used was a well-cleaned thin plate of Cu-Sn alloy (80% Cu and 20% Sn) of size 3  $\times$  2.5 sq. cm. A thin plate (5  $\times$  2.5 cm. approx.) of Cu (99.5%) serving as the cathode was first rendered free from grease by dipping it in a hot 10% caustic soda solution for a few minutes and then washing it with water; it was next immersed in moderately strong nitric acid to remove the surface scale. The plate was then washed with distilled water and finally with alcohol, dried and weighed accurately when necessary. A copper coulometer was used to give the measure of the quantity of electricity passed through the electrolyte. The coulometer solution was prepared according to Oettel's recommendations (*Chem. Ztg.*, 1893, **17**, 543). The current was obtained from 220 volts D. C. mains; the circuit consisted of an electrolyte bath, copper coulometer, a precision type milliammeter

and an adjustable resistance in series, and a voltmeter connected across the electrodes in the bath.

Two stock solutions were prepared : (A) by dissolving Merck's pure sample of  $\text{Cu}(\text{CN})_2$  (62.8 g.) and  $\text{NaCN}$  (137.2 g.) in 1000 c. c. of distilled water ; (B) by dissolving  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  (168.25 g.) and  $\text{NaOH}$  (200 g.) in 1000 c.c. of water. In all the following experiments these stock solutions were used after mixing the requisite quantities of (A) and (B), and with the appropriate additions of the other materials used in this work. To investigate the optimum conditions for a smooth, bright and adherent deposit of bronze the influence of the following factors has been studied over a wide range :

1. Electrolytic concentration in terms of metal ion content (Table IA). 2. Time (Table IB). 3. Current density (Table II). 4. Temperature (Table III). 5. Addition agents (Table IV).

The nature of the alloy deposit obtained in each of these experiments is also recorded as examined with a microscope. The cathode efficiency was calculated by the relation,

$$\% \text{Cathode efficiency} = \frac{100 \times \text{actual amount of the alloy deposited}}{\text{theoretical amount of the deposit}}.$$

TABLE IA

*Variation of the concentration of the electrolyte.*

C. D. = 0.76 amp./dm<sup>2</sup>. Time = 20 minutes Temp. of the bath =  $60 \pm 2^\circ$ . Interelectrode distance = 1 cm  $p_H = 12.5$  approx. Vol. of electrolyte = 200 c. c.

Metal ion conc.		Nature of deposit.
Copper.	Tin	
0.89001 g.	1.1388 g	Uniform, adherent and red coloured deposit with coarse grain structure
0.89001	1.7082	Good, bright and improved deposit with fine grain structure
0.89001	2.2777	Very good, bright, silvery, smooth, adherent and uniform deposit with fine grain structure
0.89001	2.8471	Deposit becomes dull white, probably due to more of Sn being deposited.

TABLE IB

*Variation of time.*

Metal ion conc : Cu = 0.89001 g. Sn = 2.2777. C. D. = 0.76 amp./dm<sup>2</sup>. Temp. =  $60 \pm 2^\circ$ . Interelectrode distance = 1 cm.  $p_H = 12.5$  approx. Vol. of electrolyte = 200 c.c.

Time.	Nature of deposit.
5 min.	Irregular crystals, red and shining deposit.
10	Deposit shining and lustrous, fine grained and of uniform structure.
15	Deposit bright, silvery, smooth, adherent and uniform
20	Still improved and highly satisfactory deposit.
25	Deposit shows tendency to peel off and to become spongy and powdery.
30	Deposit becomes black and being non-adherent, falls to powder on mere tapping the plate.

TABLE II

*Effect of current density.*

Metal ion conc : Cu=0.89001 g. Sn=2.2777 g. Interelectrode distance=1 cm  
 Temp. of the bath =  $60^{\circ} \pm 2^{\circ}$ . Time=20 mins  $p_n=12.5$  approx. Vol. of electrolyte  
 = 200 c.c.

C. D. (amp./dm <sup>2</sup> )	Wt of alloy deposit.		Cathode efficiency.	Nature of deposit
	Obs.	Calc.		
0.64	0.0236g.	0.0614g.	38.4%	Reddish deposit, more of copper
0.68	0.0339	0.0653	52.0	Deposit becomes reddish white
0.72	0.0420	0.0691	60.8	Smooth, adherent, dull white deposit.
0.76	0.0467	0.0730	62.5	Good, bright, silvery, smooth, adherent deposit with fine grained structure
0.80	0.0470	0.0768	61.2	Deposit blackens in colour, less adherent with crevices.
0.84	0.0477	0.0806	59.2	Non-uniform deposit, has tendency to peel off, deep crevices

TABLE III

*Effect of temperature.*

Metal ion conc : Cu=0.89001 g. Sn=2.2777 g. Interelectrode distance=1 cm.  
 Temp. of the bath =  $60^{\circ} \pm 2^{\circ}$ . Time=20 mins.  $p_n=12.5$  approx. Vol. of electrolyte  
 = 200 c.c.

Temp.	Wt. of alloy deposit		Cathode efficiency.	Nature of deposit
	Obs.	Calc.		
20°	0.0234 g.	0.0730 g.	32.1%	Smooth, bright, dull yellow deposit.
30°	0.0322	0.0730	44.1	Deposit of the same nature, but of golden yellow colour like brass.
40°	0.0367	0.0730	50.7	Do
50°	0.0418	0.0730	57.3	Deposit becomes reddish yellow in colour.
60°	0.0456	0.0730	62.49	Smooth, bright, silvery, adherent and uniform deposit with fine structure.
70°	0.0449	0.0730	61.6	Slightly burnt deposit.
80°	0.0443	0.0730	60.7	Burnt deposit.

TABLE IV

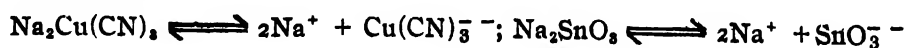
*Effect of addition agent.*

Metal ion conc : Cu=0.89001 g. Sn=2.2777 g. Interelectrode distance=1 cm.  
 Temp. of the bath=60°±2°. Time=20 min.  $p_H$ =12.5 approx. Vol. of electrolyte  
 =200 c.c.

Addition agent (A).	Amount of (A) in 1000 c.c. of soln.	Wt. of alloy deposit		Cathode efficiency	Nature of deposit.
		Obs.	Calc.		
Glycerol	5 c.c.	0.0156 g		62.5%	Satisfactory deposit of bronze.
	10	0.0451		62.2	Deposit slightly turns yellow.
	20	0.0451	0.0730 g.	62.2	Yellow colour increases.
	30	0.0450		61.7	Yellow, brass coloured deposit.
NaCl	5 g.	0.0456		62.5	Bright, silvery, adherent and uniform deposit.
	10	0.0458		62.7	Improved deposit.
	20	0.0464	0.0730 g.	63.4	" "
	30	0.0478		65.6	" "
	40	0.0471		64.9	Deposit becomes dull and dark.
	50	0.0466		63.7	Increasingly dark deposit.
H <sub>2</sub> O <sub>2</sub>	5 c.c.	0.0156		62.5	Good deposit.
	10	0.0462		63.3	Deposit improves in brightness and uniformity.
	20	0.0480	0.0730 g	65.8	Still further improvement in the deposit.
	30	0.0486		66.5	Do
	40	0.0484		66.18	Do
	50	0.0480		65.9	Deposit shining and uniform, but slightly blackening effect.

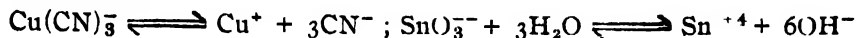
## DISCUSSION

The results in Table I A show that silvery, bright, lustrous and adherent deposit with fine grained structure is obtained from the bath solution containing the metal ion concentration : Cu, 0.89001 g., Sn, 2.2777 g. at the C.D. employed ; stronger and dilute solutions are found to yield less satisfactory results. The copper and tin ions of the plating solution are furnished by the double copper cyanide and sodium stannate ; the salts dissociate as :





This ionisation produces no copper or tin ions, but the complexes further ionise to a very small extent,

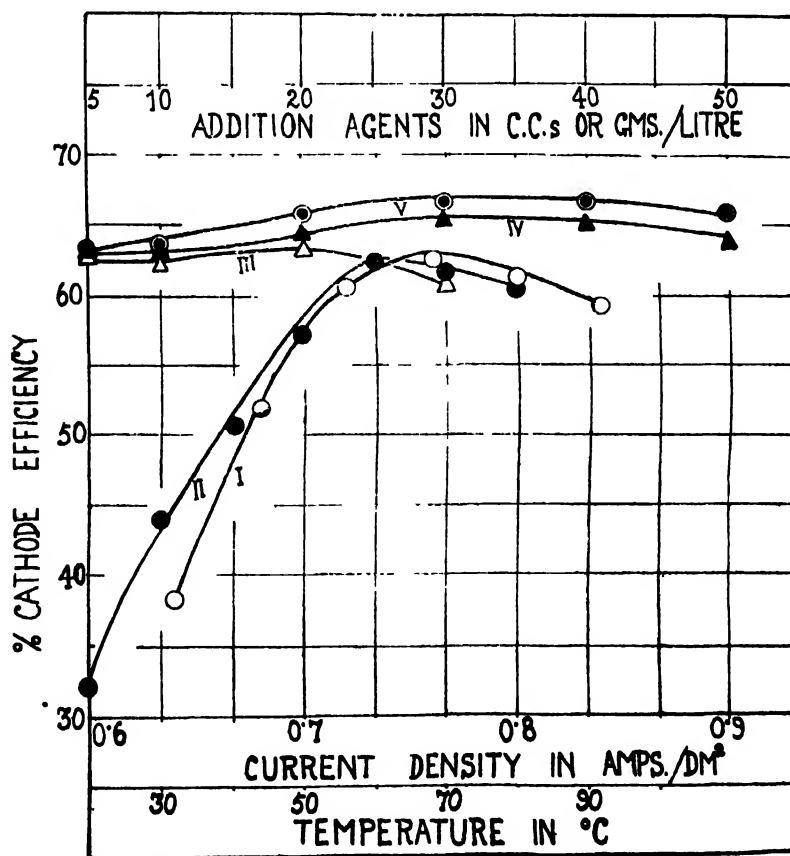


There is thus produced a favourable condition for electrodeposition; the metal ion concentration is low, but there is an inexhaustible reserve supply to replace the few metallic ions as fast as they are removed.

Our results in Table Ib show that with the increase of time (up to 20 mins.) the deposit becomes finer. Adhesivity is also improved. It is interesting to note that at constant C.D., concentration, temperature etc., the deposit, which is initially bright and adherent, tends to become, as the time elapses, loose, powdery, non-adhesive and black (cf. Table Ia). This can be attributed to the increased alkalinity of the bath due to high anodic efficiency with the progress of electrolysis and subsequent inclusion of the basic hydroxide in the cathode deposit. Kurda's findings (*Z. physikal. Chem.*, 1936, **175**, 377) lead to similar conclusions.

The data recorded in Tables II, III and IV show that the nature and magnitude of an electrodeposit is influenced by a number of physicochemical factors. These are discussed conveniently in respect of cathode efficiency which is 100 % under ideal

FIG. 1



conditions. Its diminution is chiefly due to the occurrence of side reactions, e.g., evolution of hydrogen at the cathode, or the formation of molecular or ionic complexes in the conducting system. The results in Table II (cf. curve I in Fig. 1) show that at constant values for concentration and temperature the current density exerts a pronouncedly marked influence on cathode efficiency of the bronze deposition which varies within wide limits from 38.4% at C.D. 0.64 amp./dm<sup>2</sup> to 62.5% at C.D. 0.76 amp./dm<sup>2</sup>. Very low efficiency at low C.D. is ascribable to the appreciable part of the current being utilised in discharging hydrogen at the cathode. With increase in C.D. up to 0.76 amp./dm<sup>2</sup> this evolution is appreciably inhibited due to the corresponding increase in the hydrogen overvoltage; with further increase in C.D. (0.76 amp./dm<sup>2</sup> to 0.84 amp./dm<sup>2</sup>) the efficiency diminishes obviously due to hydrogen evolution, caused by a rapid depletion of the metal in the cathode film during electrolysis. At low C.D. only copper is deposited at the cathode since the normal electrode potential of copper  $\Pi_{Cu}$  is considerably greater than  $\Pi_{Sn}$  in these solutions. With the increase in C.D. and temperature the deposition potentials of copper and tin from cyanide and alkaline stannate solution approach one another very closely. At C.D. 0.76 amp./dm<sup>2</sup> and 60°, the simultaneous deposition of the two metals is possible. Hence in order to obtain the alloy deposit, the C.D. over the whole cathode must not be less than 0.76 amp./dm<sup>2</sup> and the temperature of the bath must be more than 60° (Table III).

From a study of the data shown in Table III (cf. curve II, Fig. 1) at constant C.D. the quality of the deposit is seen to improve by increasing the temperature up to a certain extent (about 60°) and to deteriorate at higher temperature (80°). The cathodic efficiency also increases with rise in temperature steadily up to 60° and then slows down and remains almost constant at higher temperatures. Increase of temperature has two opposing effects: in the first place it favours the diffusion and tends to produce a uniform and fine grained deposit, but, on the other hand, it decreases the velocity of the crystal growth and thus fosters the formation of coarse deposits. At moderate temperature the influence of the first factor is generally predominating, but at higher temperatures the second is increasingly operative.

The data recorded in Table IV show that there is no precise relation of the cathode efficiency with the proportions of an addition agent in the electrolytic bath. In presence of NaCl and H<sub>2</sub>O<sub>2</sub>, bright, lustrous deposits are obtained with increased efficiency (curves IV and V respectively, Fig. 1), possibly due to hydrogen evolution at the cathode being considerably arrested; their increased concentration, however, produces dark deposits. The addition in traces of glycerol (0.5%) gives satisfactory deposits but with the further addition the deposit becomes spoiled and the cathodic efficiency decreases slightly (curve III, Fig. 1).

Authors are highly indebted to Dr. S.S. Joshi, for suggesting the problem and giving valuable help and criticism during this investigation.

## ESTIMATION OF BISMUTH. PART VIII. GRAVIMETRIC ANALYSIS WITH PHENYLARSONIC ACID

BY ANIL KUMAR MAJUMDAR AND RAMENDRA NATH SEN SARMA

With the reagent phenylarsonic acid, bismuth can be estimated up to a  $p_H$  as low as 2, and in presence of nitric acid over a  $p_H$  range of about 2 to 3, it can be separated from zinc, manganese, nickel, cobalt, alkalis, alkaline earths, etc. Zinc coprecipitates at a  $p_H$  over 3. Bismuth-manganese separation can also be undertaken in presence of ammonium acetate-acetic acid buffer without adding cyanide. The method for the separation of bismuth from lead has been recommended with a little modification to avoid tedious purification procedure.

The reagent phenylarsonic acid was used for the estimation of bismuth in presence of a large number of elements (Majumdar, this *Journal*, 1944, **21**, 119, 187, 188). There bismuth could not be separated from zinc and manganese in presence of cyanide due to instability of the cyanide complexes of those two elements under the conditions of the experiments. In a subsequent paper (Majumdar, *ibid.*, 1945, **22**, 313) it has been shown that bismuth can also be estimated in presence of dilute nitric and acetic acids. In this paper a study of the  $p_H$  ranges over which bismuth can be accurately estimated and, if possible, its separation from other elements at lower  $p_H$  ranges has been made. Moreover, the method suggested for the separation of bismuth from lead (Majumdar, *ibid.*, 1944, **21**, 119) has been modified to avoid the tedious procedure which is time consuming because of the slow addition of ammonium acetate solution.

During this investigation it was found that bismuth could be accurately estimated up to a  $p_H$  as low as about 2, and that during a bismuth-zinc separation, zinc coprecipitates at a  $p_H$  over 3 and that bismuth could be separated from zinc, manganese, nickel, cobalt, alkalis, alkaline earths, etc. in presence of nitric acid and that bismuth could also be separated from manganese in presence of ammonium acetate-acetic acid buffer without the addition of cyanide. As phenylarsonic acid does not produce any precipitate with the salts of alkalis and alkaline earths, the estimation of bismuth may further be conducted in their presence.

### EXPERIMENTAL

**Reagents and Standard Solutions.**—Except where specifically mentioned, the chemicals used were all of reagent quality. Reagents were (i) prepared and recrystallised phenylarsonic acid of m. p.  $157^\circ$ , (ii) a 10% solution of ammonium acetate in water, (iii) a 2N-acetic acid solution, (iv) a 65% solution of nitric acid, (v) ammonia solution prepared by passing ammonia gas through cold water.

Standard solutions of bismuth, nickel and cobalt were prepared in the same way and from the same reagents as was reported in an earlier paper (Majumdar, this *Journal*, 1944, **21**, 119). Bismuth content of its standard solution was further checked by estimating as phenylarsonate (*loc. cit.*).

Metallic lead was dissolved in nitric acid and diluted with water to a definite volume and the lead content per c. c. of the solution was determined as sulphate.

A manganese nitrate solution was prepared from manganese carbonate of B. D. H. and by the pyrophosphate method its manganese content was determined from a measured quantity of the solution.

A solution of zinc nitrate was prepared from metallic zinc and the zinc content per c.c. of the solution was determined by the pyrophosphate method.

#### *Analytical Procedure.*

*Study of  $p_H$  ranges.*—For the study of the lower  $p_H$  range over which bismuth could be completely precipitated, 5 c. c. of the standard bismuth nitrate solution were evaporated to dryness on a water-bath. The residue was dissolved by the addition of a few drops of concentrated nitric acid (65%). 1% Solution of phenylarsonic acid (10 c.c.) in water was added to the solution which was then diluted to about 250 c. c. The mixture was then heated to boiling with stirring till the precipitate became crystalline. The precipitate was filtered, washed, dried and weighed exactly according to the method reported in a previous paper (*loc. cit.*). The  $p_H$  of the filtrate from the precipitation of bismuth was measured in each test by means of the quinhydrone electrode. The results are given in Table I.

TABLE I

No.	Bi taken.	Wt. of ppt.	Bi found	$p_H$ .	Error.
1	0.0289 g.	0.0592 g.	0.0290 g	4.6	+0.0001 g.
2	0.0289	0.0588	0.0288	3.43	-0.0001
3	0.0232	0.0476	0.0233	3.2	+0.0001
4	"	0.0476	0.0233	2.7	+0.0001
5	"	0.0472	0.0231	2.3	-0.0001
6	0.0289	0.0590	0.0289	2.3	Nil
7	0.0232	0.0472	0.0231	2.0	-0.0001
8	"	0.0474	0.0232	2.1	Nil
9	"	0.0474	0.0232	2.1	Nil
10	"	0.0468	0.0229	1.95	-0.0003
11	"	0.0466	0.0228	1.9	-0.0004
12	"	0.0468	0.0229	1.85	-0.0003

By varying the amounts of nitric acid (1-2 drops to 5-6 drops) used in the dissolution of the dried residue, the hydrogen-ion concentration of the solutions was varied.

*Separation of Bismuth from Zinc*

For the estimation of bismuth in presence of zinc from a nitric acid solution containing both the metals and free form chloride, sulphate and other interfering elements, the procedure as described above was followed. But for the study of the coprecipitation of zinc, to the nitric acid solution of metals were added a few c. c. (15-16 c. c.) of the reagent solution (1%) and the solution was neutralised with dilute ammonia, using thymol blue as indicator (acid range, 1.2 to 2.8). A few drops of dilute ammonia were then added in excess and the solution was diluted to 250 c. c., heated to boiling, etc. as mentioned above. To study the effect of different  $p_H$ , the amount of excess ammonia added was varied. Results are shown in Table II.

TABLE II

No.	Bi taken.	Zn taken.	Wt. of ppt.	Bi found.	$p_H$ .	Error
1	0.0289 g.	0.05025 g.	0.0592 g.	0.0290 g.	...	+0.0001 g.
2	0.0289	0.05025	0.0590	0.0289	..	Nil
3	0.0289	0.1005	0.0588	0.0288	2.4	-0.0001
4	0.0289	0.1005	0.0593	0.0291	2.6	+0.0002
5	0.0232	0.15075	0.0476	0.0233	2.4	+0.0001
6	0.0232	0.15075	0.0474	0.0232	2.35	Nil
7	0.0232	0.2010	0.0474	0.0232	2.3	Nil
8	0.0232	0.2010	0.0472	0.0231	2.25	-0.0001
9	0.0232	0.3015	0.0474	0.0232	2.3	Nil
10	0.0232	0.3015	0.0474	0.0232	2.4	Nil
11	0.0232	0.05025	0.0476	0.0233	3.1	0.0001
12	0.0232	0.1005	0.0472	0.0231	3.1	-0.0001
13	0.0232	0.1005	0.1940	0.0952	4.1	+0.0720
14	0.0232	0.05025	0.0670	0.0329	3.55	+0.0097
15	0.0232	0.05025	0.0900	0.0442	3.7	+0.0210

*Separation of Bismuth from Manganese, Nickel and Cobalt*

Here the procedure followed was the same as has been described under the "Study of  $p_H$  ranges". Results are given in Table III.

TABLE III

No.	Metals taken.		Wt of ppt.	Bi found.	pH.	Error
1	Bi	0.0232 g.				
	Mn	0.0408	0.0474 g.	0.0232 g.	2.2	Nil
2	Bi	0.0232				
	Mn	0.0408	0.0472	0.0231	2.2	-0.0001 g.
3	Bi	0.0232				
	Mn	0.0817	0.0474	0.0232	2.1	Nil
4	Bi	0.0232				
	Mn	0.0817	0.0474	0.0232	2.1	Nil
5	Bi	0.0232				
	Mn	0.1225	0.0474	0.0232	2.14	Nil
6	Bi	0.0232				
	Mn	0.1225	0.0472	0.0231	2.10	-0.0001
7	Bi	0.0232				
	Mn	0.1634	0.0475	0.0233	2.14	+0.0001
8	Bi	0.0232				
	Mn	0.1634	0.0474	0.0232	2.2	Nil
9	Bi	0.0232				
	Ni	0.2012	0.0474	0.0232	2.4	Nil
10	Bi	0.0232				
	Ni	0.1006	0.0472	0.0231	2.2	-0.0001
11	Bi	0.0232				
	Co	0.1140	0.0472	0.0231	2.3	-0.0001
12	Bi	0.0232				
	Co	0.228	0.0474	0.0232	2.2	Nil

*Separation of Bismuth from Manganese in presence of Ammonium  
Acetate-acetic Acid Buffer*

After the addition of 10 to 12 c.c. of the reagent solution (1%) to the nitric acid solution of bismuth and manganese, it was neutralised with dilute ammonia (using Wesselow's indicator) and acidified with 2 c.c. of 2-N-acetic acid. Ammonium acetate solution (10 c.c., 10%) was then added to the solution which was then diluted to 250 c.c., heated to boiling etc. as described under the "Study of pH ranges". The results are given in Table IV.

TABLE IV

No.	Bi taken.	Mn taken.	Wt. of ppt.	Bi found	$\mu$ .	Error.
1	0.0232 g.	0.0408 g.	0.0472 g.	0.0231 g.	5.0	- 0.0001 g
2	0.232	0.0408	0.0474	0.0232	5.1	Nil
3	0.0232	0.1225	0.0472	0.0231	4.95	-0.0001
4	0.0232	0.1634	0.0474	0.0232	5.0	Nil

*Separation of Bismuth from Lead*

A nitric acid solution of bismuth and lead was evaporated to dryness on a water-bath. The dried residue was dissolved by treatment with a few drops of nitric acid and to it were added 3 to 4 c.c. of a 5% solution of the reagent phenylarsonic acid. If any precipitate formed due to the addition of the reagent, that was also dissolved with the addition of a few drops of nitric acid. To this solution was then added an excess of ammonium acetate solution and diluted to 250 c.c., heated to boiling with stirring till the precipitate was crystalline. The precipitate was then filtered, washed, dried and weighed as usual (*loc. cit.*). Results are given in Table V.

TABLE V

No.	Bi taken.	Pb taken.	Ammonium acetate.	Wt. of ppt	Bi found.	Error.
1	0.0289 g.	0.0491 g.	10 c.c.	0.0592	0.0290 g.	+0.0001 g.
2	0.0289	0.0491	50	0.0590	0.0289	Nil
3	0.0289	0.0982	50	0.0590	0.0289	Nil
4	0.0289	0.0982	50	0.0592	0.0290	+0.0001
5	0.0289	0.1473	50	0.0590	0.0289	Nil
6	0.0289	0.1473	50	0.0592	0.0290	+0.0001
7	0.0289	0.1964	50	0.0588	0.0288	-0.0001
8	0.0289	0.1964	60	0.0590	0.0289	Nil
9	0.0289	0.2946	70	0.0592	0.0290	+0.0001
10	0.0289	0.2946	70	0.0590	0.0289	Nil
11	0.0578	0.0491	50	0.1184	0.0580	+0.0002
12	0.0578	0.0491	50	0.1182	0.0580	+0.0002

## C O N C L U S I O N

Phenylarsonic acid can be suitably used as a reagent for the estimation of bismuth in presence of a large number of elements. Thus, in presence of nitric acid, over the  $p_H$  range 2 to 3, bismuth can be separated from zinc, manganese, nickel, cobalt, alkalis and alkaline earths. In presence of ammonium acetate-acetic acid buffer, it was separated from alkalis, alkaline earths, lead, mercury, manganese, thallous and sulphate ions; also under the same condition it was separated from silver, copper, cadmium, cobalt and nickel using potassium cyanide as a complex forming agent. Its separation from zirconium, thorium and tin depends upon the precipitation of those metals in stronger acid solutions when bismuth phenylarsonate remains in solution.

The authors' best thanks are due to the authorities of the College for giving them facilities for this work.

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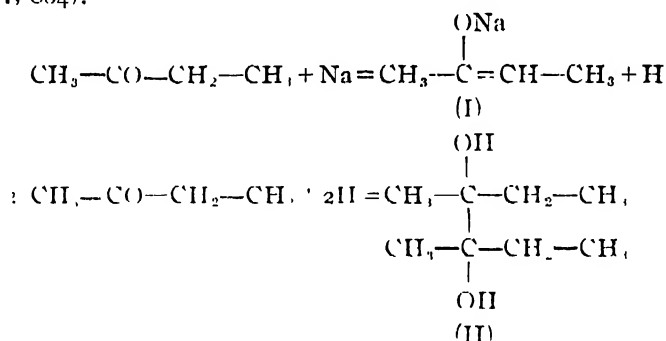


## ALKYLATION OF KETONES

BY R. R. AGARWAL AND S. S. DESHAPANDE

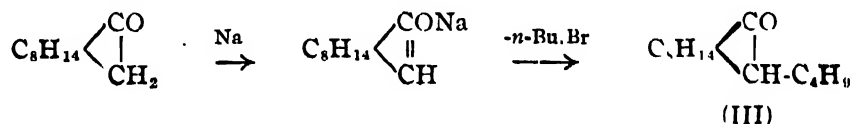
A suitable method for alkylation of ketones is to prepare first oxymethylene compound of the ketone (2-formyl ketone). By treating sodium derivative of the 2-formyl ketone with the alkyl halide, 2-formyl 2-alkyl ketone is formed which on ketonic hydrolysis yields 2-alkyl ketone. The process is illustrated by the synthesis of 2-ethylcyclohexanone from cyclohexanone.

If a 1:3-diketone  $\text{—CO—CH—CO—}$  in the form of its sodium enolate  $\text{—}\overset{\text{NaO}}{\underset{|}{\text{C}}}=\text{C—CO—}$  is treated with an alkyl halide, alkylation takes place in 2-position. A simple ketone  $\text{—CO—CH—}$  should similarly be capable of being alkylated in 2-position if its sodium enolate  $\text{—}\overset{\text{NaO}}{\underset{|}{\text{C}}}=\text{C—}$  could be obtained. Generally, by the action of sodium on a ketone some amount of its sodium enolate is formed, but simultaneously sodium compounds of secondary reaction products are also formed. For instance, by the action of sodium on methylethyl ketone, not only the sodium enolate of the ketone (I) but also sodium compound of 3:4-dimethylhexane-diol-3:4 (II) is produced, obviously by reduction of the ketone by hydrogen evolved in the formation of sodium enolate (I) (Braun, *Monats*, 1906, 27, 804).

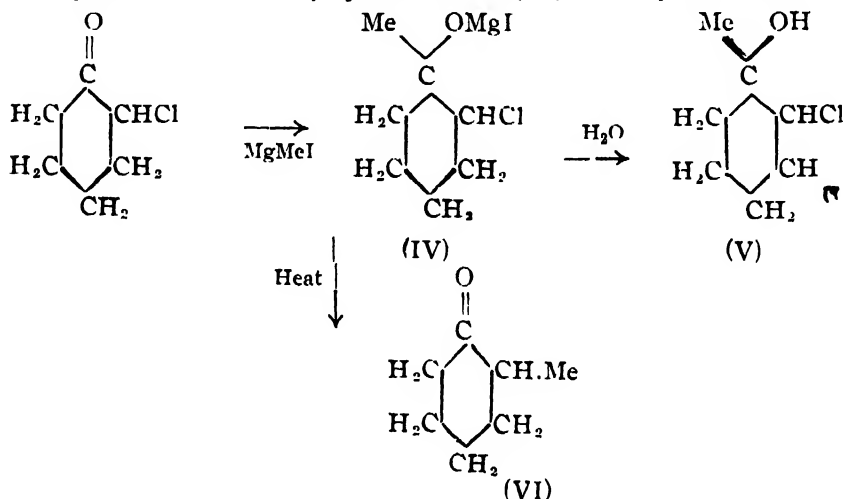


By the action of alkyl halides on sodium compounds formed from cyclohexanone, menthone, carvone and methylethyl ketone, we failed to obtain any appreciable amount of the corresponding 2-alkyl ketones.

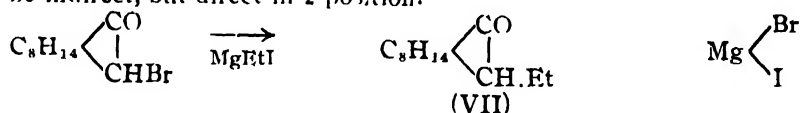
Beckmann (*J. prakt. Chem.*, 1897 ii, 55, 35) describes that the so-called 'sodium camphor', obtained by the action of sodium on camphor, dissolved in ether, contains also sodium borneol and sodium isoborneol. By keeping *l*-camphor dissolved in dry ether in contact with sodium dust at room temperature, we found that the sodium practically went into solution. On adding bromine to the 'sodium camphor', thus formed, we obtained an excellent yield of 2-bromo-*l*-camphor. The 'sodium camphor', therefore consisted mostly of the sodium enolate of camphor, and as expected, when it was treated with *n*-butyl bromide it gave us 2-*n*-butyl-*l* camphor (III).



An indirect formation of a 2-alkyl ketone through 2-chloro-ketone has been shown by Tiffeneau and Tchoubar (*Compt. rend.*, 1934, **198**, 941). These authors have shown that when magnesiummethyl iodide is added at room temperature to 2-chlorocyclohexanone, the reaction takes place at the keto group rather than at the chlorine of the ketone, and organo-magnesium derivative (IV) is formed, from which by decomposition with water 2-chloro-1-methylcyclohexanol (V) is obtained. If, however, (IV) is boiled in ether, magnesium halide separates, the methyl group migrates to 2-position, and 2-methylcyclohexanone (VI) is finally obtained.

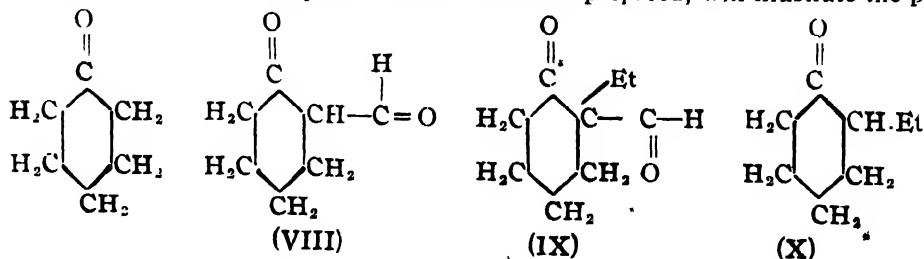


Working with 2-bromo-1-camphor we found that when magnesiummethyl iodide was added to its ethereal solution at ice temperature, magnesium halide began to separate almost immediately and on completion of separation we obtained 2-ethyl-1-camphor (VII) from the filtrate. In this case, at any rate, the alkylation of ketone does not seem to be indirect, but direct in 2-position.



As, however, 2-chloro-ketones cannot be obtained easily, this method is not of general utility for preparing 2-alkyl ketones.

A method which we have found reliable and convenient for obtaining 2-alkyl ketones is through 2-formyl ketones (oxymethylene ketones). The latter are obtained by treating ketones with ethyl formate and sodium. The preparation of 2-ethylcyclohexanone, one of the 2-alkylated ketones we have prepared, will illustrate the process.



2-Formylcyclohexanone (oxymethylene cyclohexanone) (VIII), prepared from cyclohexanone and ethyl formate, was treated with sodium ethylate, and the sodium derivative of the 1:3-dicarbonyl compound reacted with ethyl iodide to give 2-formyl-2-ethylcyclohexanone (IX). By ketonic hydrolysis of (IX) the formyl group was removed and 2-ethylcyclohexanone (X) was obtained.

Paranjpye, Bhide and Nargund prepared 2-formyl-2-methylcyclohexanone, in crude form which they could not purify by distillation (*Nature*, 1944, **153**, 141). They reported that their crude product was optically active having specific rotation  $[\alpha]_D = -26.22^\circ$ . Such an asymmetric synthesis being highly improbable the process of methylation of 2-formylcyclohexanone was examined by O'Gorman (*J. Amer. Chem. Soc.*, 1944, **66**, 1041) and by Cornforth, Cornforth and Dewar (*Nature*, 1944, **153**, 317). In none of these experiments was the methylation product found to be optically active. The higher homologue, 2-formyl-2-ethylcyclohexanone (IX) in our case, was found to be completely inactive, as expected.

#### EXPERIMENTAL

*Sodium l-camphor and 2-Bromo-l-camphor*—Sodium dust, prepared by melting 2.3 g. (1 atom) of sodium under boiling xylene and vigorous shaking, was covered by dry ether and kept cool. A solution of *l*-camphor (15.2 g., 1 mol.) in dry ether was then gradually added. The mixture was allowed to remain at room temperature for 6 days when most of the sodium dissolved as 'sodium camphor', a small amount of brown mass remaining outside.

To the 'sodium camphor', kept at  $0^\circ$ , was added gradually a solution of bromine (16 g.) in dry carbon tetrachloride. Bromine was rapidly absorbed and sodium bromide separating was removed by filtration. The filtrate on being freed from slight excess of bromine by alkali was washed and dried and the solvent removed. From the residue unchanged camphor was removed by distilling up to  $215^\circ$ . The solid residue obtained on cooling was crystallised from dilute alcohol in plates, m. p.  $76^\circ$ , yie'd 16 g. (70% of theory). It was identified as *l*-bromocamphor from its melting point and bromine content.

*2-n-Butyl-l-camphor* (III).—To 'sodium camphor', prepared as described above, was added *n*-butyl bromide (13.7 g., 1 mol.). The mixture was gently refluxed on a water-bath for 7 hours when the reaction became nearly neutral and sodium bromide separated. On cooling, the mixture was made slightly acid, the ether layer was washed and dried and the solvent removed. On distilling the remaining liquid 4.5 g. passed between  $50^\circ$  and  $90^\circ$  at 90 mm. The remainder solidified in the distilling flask on cooling. The solid freed from adhering liquid weighed 7 g. and crystallised from dilute alcohol in feathery needles, m. p.  $188^\circ$  (*l*-camphor, m. p.  $175^\circ$ ):  $[\alpha]_D^{25}$  in alcohol =  $-32.1^\circ$ . [Found: C, 80.6; H, 10.8.  $C_{14}H_{24}O$  (butyl camphor) requires C, 80.8; H, 11.5 per cent.  $C_{10}H_{16}O$  (camphor) requires C, 78.9; H, 10.5 per cent]. 2-*n*-Butyl-*l*-camphor forms a 2:4-dinitrophenylhydrazone, m. p.  $169^\circ$ .

*2-Ethyl-l-camphor* (VII).—Grignard reagent (prepared from Mg, 1.2 g. and ethyl iodide in dry ether) was gradually added to a cooled solution of 9.2 g. of 2-bromo-*l*-camphor in dry ether. The whole was allowed to remain at ice temperature over-

night. Greyish white magnesium halide separated. The reaction was completed by warming for a few minutes. The product was poured into dilute hydrochloric acid, the ether layer was washed and dried and the solvent removed. A white solid free from bromine was left. It was crystallised from dilute alcohol, m. p.  $148^{\circ}$ ;  $[\alpha]_D = -128.7^{\circ}$  in alcohol. (Found: C, 79.2; H, 10.8.  $C_{12}H_{20}O$  requires C, 80.0; H, 11.0 per cent). It forms a 2:4-dinitrophenylhydrazone, m. p.  $188^{\circ}$ .

2-Ethyl-*d*-camphor was prepared by Boubigny (*Chem. Zentr.*, 1886, II, 409) by treating sodium *d*-camphor with ethyl iodide in toluene at  $60^{\circ}$ , and is described as a liquid, b. p.  $226^{\circ}$ - $231^{\circ}$ . Since the corresponding *l*-stereoisomer (di-*l*-stereoisomeride of the above) prepared by us was a solid, it became necessary to confirm its isomerism with the above by preparing it by Boubigny's method using *l*-camphor instead of *d*-camphor. The product obtained was a mixture of *l*-camphor and 2-ethyl-*l*-camphor. Separation was effected by repeated crystallisation followed by sublimation, the former subliming more readily than the latter. 2-Ethyl-*l*-camphor, thus obtained, was finally purified by crystallisation, m. p.  $148^{\circ}$  and it formed a 2:4-dinitrophenylhydrazone, m. p.  $188^{\circ}$ . Thus, the 2-ethyl-*l*-camphor, prepared from sodium *l*-camphor and ethyl iodide, was found to be identical with the product obtained from *l*-bromocamphor and magnesium ethyl iodide. 2-Methylation of *d*-camphor through sodium *d*-camphor was effected with great difficulty by Haller (*Compt. rend.*, 1809, **148**, 1645), the reaction product being always a mixture of *d*-camphor and methylated *d*-camphor.

2-Formyl-2-ethylcyclohexanone (IX) from Formylcyclohexanone (VIII).—To sodium ethylate, prepared from sodium (1 g.) and absolute alcohol (35 c.c.), formylcyclohexanone (6 g.) was gradually added under cooling, and then ethyl iodide (6.9 g.) was added. The mixture was refluxed on a water-bath for 8 hours when it gave nearly neutral reaction. On removing excess of alcohol and acidifying, a deep green liquid resulted which was extracted with carbon tetrachloride. After washing, drying and removing the solvent the remaining liquid distilled at  $81^{\circ}$ - $84^{\circ}/3\text{mm.}$ , yield 3.5 g. (Found: C, 69.6; H, 9.5.  $C_9H_{14}O_2$  requires C, 70.1; H, 9.1 per cent). The compound gives a blue colour with ferric chloride and forms a semicarbazone, m. p.  $145^{\circ}$  (semicarbazone of 2-formylcyclohexanone, m. p.  $231^{\circ}$ ).

Ketonic Hydrolysis of 2-Formyl-2-ethylcyclohexanone: Formation of 2-Ethylcyclohexanone (X).—Caustic potash (15 c.c., 10%) was added to 2-formyl-2-ethylcyclohexanone in a small flask, and the mixture was gently refluxed on a sand-bath for 5 hours when a reddish oily layer was seen floating over aqueous alkali. This was extracted with ether, the solvent washed, dried and removed. The residual liquid distilled at  $90^{\circ}/65\text{ mm.}$

2-Ethylcyclohexanone was prepared by Lescr (*Compt. rend.*, 1806, **141**, 1033) by the action of hot alkali on 1-ethyl-1-acetylcyclohexanone and is described as liquid, b. p.  $65^{\circ}/10\text{ mm.}$  (semicarbazone, m. p.  $157^{\circ}$ ). (Found: C, 75.9; H, 11.4.  $C_8H_{14}O$  requires C, 76.2; H, 11.1 per cent).

2-Ethylcyclohexanone is a colorless liquid with camphor-like odour. It forms a semicarbazone, m. p.  $155^{\circ}$ .

## THORIUM. ITS SEPARATION AND ESTIMATION. THE IODATE METHOD

By M. VENKATARAMANIAN AND BH. S. V. RAGHAVA RAO

It is shown that thorium can be estimated by precipitation with iodic acid in nearly neutral solutions and may also be freed from uranium. In 4*N*-nitric acid solution iodic acid fixes thorium from cerite earths in two precipitations. This method is an improvement on the classical method in that the precipitate can be weighed directly. Thorium in monazite has been successfully determined in this way.

The best known method for the separation of thorium from the cerite earths is that of Meyer and Speter (*Chem. Ztg.*, 1910, **34**, 306) but it suffers from the serious disadvantage that the composition of the precipitate is uncertain and consequently a direct determination by weighing the precipitate is not possible. Recently, however, Moeller and Fritz (*Chem. Rev.*, 1948, **42**, 63) have shown that the precipitate is the normal iodate but difficulties arise in washing the same free of adsorbed iodate and nitric acid, chief of which are the solubility of the precipitate and its hydrolysis in the comparatively large quantities of water necessary to remove the sparingly soluble potassium iodate. As a result, the thorium recovery in their experiments is about 99%. Prior to the appearance of this publication, we carried out a number of experiments employing iodic acid, for, preliminary studies with potassium iodate indicated that in neutral solution the precipitate approximated to a basic iodate of the composition  $\text{ThO}_2 \cdot 2\text{Th}(\text{IO}_3)_4$ , while in the presence of acid the normal tetraiodate resulted always. Our procedure with iodic acid is not subject to the failings mentioned by Moeller and Fritz (*loc. cit.*). The removal of iodic acid is easy on account of its high solubility; and normal iodate precipitates under all conditions. We have also determined in a semi-quantitative manner the thorium loss through solubility and hydrolysis. Our conclusions are that the solubility of normal thorium iodate in water at the room temperature (about 26°) is negligibly small, as will be evident from the following simple experiment.

Moist thorium iodate (5 g.) was shaken up with 200 c.c. of water for 5 hours and filtered. The filtrate (100 c.c.) on concentration to 10 c.c. failed to give a colorimetric test capable of detecting 0.01 mg. of thorium per c.c. Thus, the quantity, if any, of thorium passing into solution is less than 0.04 mg. per 100 c.c. Error resulting from the effect of hydrolysis appears, however, to be of a higher magnitude. In a similar experiment titration with thiosulphate of the iodate ion in solution indicated a concentration of 0.8 mg. in 100 c.c. If on the other hand a mixture of equal volumes of alcohol and water is used, the hydrolysis is considerably suppressed and amounts to only a third of that in water alone. This of course does not represent the magnitude of the error in an actual determination; it is indeed much smaller. In the iodic acid procedure described below, it will be seen that there is a great simplification of the process with a substantial increase in accuracy.

## E X P E R I M E N T A L

*When Thorium is present alone or is admixed with Uranium.*—The thorium solution, if acid, is rendered neutral or but faintly acid to congo red by careful addition of dilute ammonia (potassium or sodium hydroxide is not recommended on account of the lower solubility of these iodates) and heated to 60° to 70°. A 2.5% aqueous solution of iodic acid is added in slight excess and the resulting heavy precipitate is left to settle in a warm place. This takes about 15 to 30 minutes. The supernatant liquid is poured through a Jena glass crucible No. 4, the precipitate is washed by decantation in the beaker 4 or 5 times with 0.25% iodic acid, transferred to the crucible and finally washed with 20 to 25 c.c. of cold water. On drying at 105° for 3 to 4 hours the precipitate corresponds to the composition,  $\text{Th}(\text{IO}_3)_4$ , and may be weighed as such. Some results are summarised in Table I.

TABLE I

Thorium taken.	Wt. of thorium iodate obtained	Wt. of thorium calc.	Error
0.2110 g.	0.8484 g.	0.2113 g.	+0.0003 g.
0.2110	0.8481	0.2112	+0.0002
0.2015	0.8090	0.2015	—
—	0.8083	0.2013	0.0002
—	0.8104	0.2018	+0.0003
—φ	0.8090	0.2015	—
—φ	0.8098	0.2017	+0.0002

φ In these estimations a quantity of uranyl nitrate corresponding to 0.20 g. of  $\text{UO}_3$  was present

*When Thorium is admixed with Cerite Earths.*—In neutral or faintly acid solution both thorium and the cerite earths are precipitated, while if the solution is too acid (6N and above) the thorium is incompletely precipitated. An extended investigation has shown that the acidity of the solution should remain at a minimum  $p_H$ ; the iodate ion concentration also should at least approximately be regulated. A 3.5% solution of iodic acid in 5N-nitric acid yields the best results. About 150 c.c. of the reagent are necessary to precipitate completely 0.1 to 0.2 g. of thorium. The procedure is as follows:

To the thorium solution (10 to 25 c.c.) are added in a thin stream with constant stirring about 150 c.c. of the cold reagent and the precipitate is allowed to settle for half an hour. It is then filtered through a Jena glass crucible (No.4), washed first with 0.35% iodic acid in 0.5N-nitric acid and, then with 25 to 40 c.c. of cold water. Washing with cold water is withheld when a double precipitation is resorted to. In this case the precipitate is dissolved in 25 c.c. of concentrated nitric acid and suitably diluted so as to give a solution 4 to 5 normal in nitric acid. A saturated solution of 5 g. of iodic acid in water is then added. It is important that the overall concentration of nitric acid should not fall below 4N, and the iodic acid concentration should be at least 3%. The following table shows the results obtained.

TABLE II

Wt. of $\text{ThO}_2$ taken.	Wt. of cerite earths (oxide) added.	Wt. $\text{Th}(\text{IO}_3)_4$ obtained.	Wt. of $\text{ThO}_2$ calc.	Error.
0.1140g.	—	0.4038g. $\phi$	0.1145g.	+0.0005g.
"	—	0.4035 $\phi$	0.1144	+0.0004
"	0.0280 g.	0.4032 $\phi$	0.1142	+0.0002
"	"	0.4030	0.1142	+0.0002
"	0.1402	0.4160 $\phi$	0.1179	+0.0039
"	"	0.4031	0.1141	+0.0001
"	1.1421	0.4032	0.1112	+0.0002
"	"	0.4027	0.1140	—
* Monazite				
0.0900 g.	0.4708	0.3182	0.0902	+0.0002
"	"	0.3185	0.0903	+0.0003

$\phi$  These figures refer to values obtained on single precipitation.

\* Monazite concentrate containing  $\text{ThO}_2$ , 0.0900 g., +  $\text{Ce}_2\text{O}_3$ , 0.4708 g.

## CONCLUSION

Thorium can be conveniently precipitated and estimated as  $\text{Th}(\text{IO}_3)_4$  in nearly neutral solution by using iodic acid as precipitant. This provides also a method for separating *thorium* from *uranium*.

In the presence of nitric acid, about 4N, iodic acid separates thorium completely from the cerite earths in two precipitations; the final precipitate may be weighed directly. When the quantity of cerite earths is small, less than a tenth of the thorium concentration, complete separation takes place in a single precipitation. Thorium in monazite can be accurately estimated by this method in much shorter time than in the classical iodate method.

## STUDIES ON THE FRIES REARRANGEMENT

BY A. B. SEN AND S. S. TEWARI

Fries rearrangement has been studied in the case of eight new esters of 4-ethylphenol at two different temperatures. The *ortho*-hydroxy ketones thus obtained have been characterised through their 2:4-dinitrophenylhydrazones.

Auwers and Mauss (*Annalen*, 1928, **480**, 240) obtained a 70 % yield of 2-hydroxy-5-ethylacetophenone by the Fries rearrangement of 4-ethyl phenylacetate. This reaction has been extended in this paper to eight new esters of 4-ethylphenol, viz., propionate, butyrate, caproate, heptate, caprylate, caprate, laurate and myristate, which were obtained in the usual manner by the action of the acid chlorides on 4-ethylphenol. The reaction was studied at two different temperatures, viz., 100° and 130°; an *o*-hydroxy ketone was obtained in each case and the difference in the yield of ketone formed at two temperatures was very small, the reaction being a little more rapid at 130°.

## EXPERIMENTAL

The esters were obtained by the action of the appropriate acid chloride on ethylphenol. The general method followed is outlined below.

4-Ethylphenol (0.1M) was taken in a 250 c.c. i.b. flask fitted with a reflux condenser carrying a calcium chloride tube and the appropriate acid chloride (0.11M) was added slowly to it. The reaction mixture was warmed on the water-bath until the evolution of hydrogen chloride had ceased. After cooling, the mixture was extracted with ether, washed with 1% caustic soda, then with water and dried over anhydrous sodium sulphate, the ether was distilled off and the residue distilled under reduced pressure.

TABLE I

4-Ethylphenyl esters	Reactants		Yield of ester		B.P.	Molecular formula	Analysis			
	Phenol	Acid chloride					Found C	Found H	Calc C	Calc H
Propionate	7.78	5.98	6.5 g	63.2%	130°/15mm.	C <sub>11</sub> H <sub>14</sub> O <sub>2</sub>	74.30%	7.85%	74.15%	7.86%
Butyrate	9	8.7	8.5	60.1	150°/9	C <sub>12</sub> H <sub>16</sub> O <sub>2</sub>	74.81	8.72	74.91	8.90
Caproate	11	13.3	13	65.85	166°/9	C <sub>14</sub> H <sub>20</sub> O <sub>2</sub>	76.50	9.20	76.37	9.09
Heptate	10	13.4	13	67.7	178°/11	C <sub>15</sub> H <sub>22</sub> O <sub>2</sub>	77.20	9.20	76.93	9.40
Caprylate	10	14.7	10.5	50.16	195°/12	C <sub>16</sub> H <sub>24</sub> O <sub>2</sub>	77.31	9.40	77.76	9.67
Caprate	5.05	8.3	8	70.1	226°/19	C <sub>18</sub> H <sub>28</sub> O <sub>2</sub>	78.45	10.40	78.27	10.14
Laurate	6.1	12	12.5	81.2	210°/16	C <sub>20</sub> H <sub>32</sub> O <sub>2</sub>	78.67	10.29	78.94	10.52
Myristate	6.8	15	14.6	78.9	210°/14	C <sub>22</sub> H <sub>36</sub> O <sub>2</sub>	78.80	10.80	79.52	10.84



TABLE II  
*Fries rearrangement*

4-Ethylphenyl esters.	Ester AlCl <sub>3</sub>	Temp	Ketone formed. R = ethyl, isopropyl, ethylphenyl; K = ketone	Yield.	Bp	Analysis of ketone	Dinitrophenyl M.p.	Mol. formula.	% N Found. Calc.
Propionate	3.0 g	37 g. 135°	R-ethyl-K	2.1 g. 18%	125°/11 mm.	Found %C 74.20 %H 7.71	7.85	C <sub>17</sub> H <sub>18</sub> O <sub>3</sub> N <sub>4</sub>	15.42 15.64
Butyrate	4.0	45 135°	R-butyl-K	3.0 28%	145°/10	8.50	8.90	C <sub>18</sub> H <sub>20</sub> O <sub>3</sub> N <sub>4</sub>	14.80 15.00
Caproate	4.0	45 135°	R-hexyl-K	3.3 32%	172°/10	7.52	9.22	C <sub>22</sub> H <sub>24</sub> O <sub>3</sub> N <sub>4</sub>	13.77 14.00
Heptate	4.0	45 135°	R-heptyl-K	3.2 31%	173°/9	7.10	9.31	C <sub>24</sub> H <sub>26</sub> O <sub>3</sub> N <sub>4</sub>	13.20 13.53
Caprylate	4.0	45 135°	R-octyl-K	3.2 31%	184°/11	7.41	9.30	C <sub>25</sub> H <sub>28</sub> O <sub>3</sub> N <sub>4</sub>	12.87 13.08
Caprate	3.0	2.1 135°	R-nonyl-K	2.5 22%	172°/11	7.85	10.30	C <sub>27</sub> H <sub>30</sub> O <sub>3</sub> N <sub>4</sub>	12.23 12.28
Laurate	4.5	3.5 135°	R-lauryl-K	3.1 29%	215°/13	7.87	10.10	C <sub>28</sub> H <sub>30</sub> O <sub>3</sub> N <sub>4</sub>	11.18 11.50
Miristate	5.0	3.3 135°	R-myristyl-K	3.3 30%	210 17	79.70	10.70	C <sub>28</sub> H <sub>30</sub> O <sub>3</sub> N <sub>4</sub>	10.60 10.93

The molecular weights of the ketones are the same as that of the respective esters from which they have been prepared by the Fries rearrangement.

*Fries Rearrangement of the Esters*

The Fries rearrangement was studied at two temperatures ( $100^{\circ}$  and  $130^{\circ}$ ). The general procedure followed is given below

Finely powdered anhydrous aluminium chloride ( $0.1M$ ) was taken in a 125 c.c. r.b. flask fitted with a reflux condenser carrying a dropping funnel and a calcium chloride tube, and the ester ( $0.06M$ ) was gradually added to it. The temperature was gradually raised to  $100^{\circ}$  in one experiment (water-bath) and to  $130^{\circ}$  in the other (oil-bath). The evolution of hydrogen chloride commenced at  $60^{\circ}$ . The reaction was slightly more rapid at  $130^{\circ}$ . After two hours the reaction mixture was cooled and dilute hydrochloric acid was added to the red puffy mass obtained to decompose the aluminium complex. The oil that separated was taken up in ether, washed successively with water, 1 % sodium carbonate solution and then again with water. After dehydration over anhydrous sodium sulphate the ether was distilled off and the residue distilled under reduced pressure.

The distillate gave an intense red-violet colour with ferric chloride and on addition of dilute caustic soda a yellowish red precipitate was obtained. It thus conforms to Pyman's tests for *ortho*-hydroxy ketones (Pyman, *J. Chem. Soc.*, 1930,280). The *o*-hydroxy ketones thus obtained were converted into their 2,4-dinitrophenylhydrazones which were recrystallised from glacial acetic acid. The yield of ketones at  $130^{\circ}$  is a little lower than at  $100^{\circ}$ .

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## ON THE RELATIONSHIP BETWEEN FLUIDITY OF LIQUIDS AND TEMPERATURE\*

BY ASOKE KUMAR MUKHERJEE

Starting from Batschinski's equation, an equation relating fluidity ( $\phi$ ) with the coefficient of thermal expansion ( $\alpha$ ) of a liquid has been derived which gives a linear plot for  $\phi$  against  $e^{1/T}$ . This relationship has been verified in the case of as many as 60 different liquids. From the intercept of the graph on the  $e^{1/T}$ -axis, dimensions of molecules have been calculated and compared with the values obtained from other methods. Members of the same homologous series are found to yield the same intercept in each case as has been verified with five different homologous series.

Recently Eyring (*J. Chem. Phys.*, 1936, **4**, 283; Hirschfelder, Stevenson and Eyring, *ibid.*, 1937, **5**, 896) has proposed a picture of the liquid state in which he assumes liquids to be composed of molecules and some free space divided into smaller units of an enormous number of holes, mixed together and distributed at random. From this conception of holes in liquids he has been able to deduce an equation of state for liquids similar in form to Van der Waals' equation of state, the Hildebrand and Trouton rule for vapour pressure, the entropy change on melting, the temperature coefficient of viscosity, etc. The flow of a liquid has been regarded by him as due to jump of molecules from one hole into another by the action of some shearing stress and is thus dependent on the number of such holes in a given mass of liquid. This free volume in liquids has been related to the temperature and total volume of the liquid (Eyring and Hirschfelder, *J. Phys. Chem.*, 1937, **41**, 249; Hirschfelder, *J. Chem. Ed.*, 1939, **16**, 540) and a method for its experimental determination evolved based upon the velocity of sound in the liquid medium (Kincaid and Eyring, *J. Chem. Phys.*, 1938, **6**, 620).

The first empirical relationship between fluidity ( $\phi$ ) and free volume ( $V - V_s$ ) as proposed by Batschinski (*Z. physikal. Chem.*, 1913, **84**, 643) in the equation

$$\phi = C \cdot (V - V_s) \quad (i)$$

assumes a linear relationship between the two,  $C$  being a constant and  $V$  and  $V_s$ , the molecular volumes of the liquid and solid states respectively, the latter being regarded as possessing little or no free volume.

In the present paper an attempt has been made to correlate fluidity ( $\phi$ ) with thermal expansion and free volume of the liquid. The relation thus obtained has been experimentally verified.

Let  $\alpha$  be the coefficient of thermal expansion of a liquid. Then by definition of  $\alpha$  we have,

$$\alpha = \frac{1}{V} \left( \frac{dV}{dT} \right)_P = \left( d \frac{\ln V}{dT} \right)_P \quad (ii)$$

\* A portion of the material embodied in this paper has been published as a note in the June issue, 1949 of "Science and Culture".

where  $V$ ,  $P$  and  $T$  refer to the molecular volume, pressure and the temperature in the absolute scale respectively of the liquid.

Assuming  $\alpha$  to remain constant for small ranges of temperatures and assuming also that the volume of a liquid changes continuously with temperature in accordance with its own coefficient of expansion, we get by integration

$$V = A e^{\alpha T} \quad \dots (iii)$$

where  $A$  is the integration constant

Let us assume that there is a temperature  $T_*$  in the absolute scale, where the free space in the liquid vanishes altogether. By carrying out the integration between  $T_*$  and any higher temperature  $T$  for which the volumes of the liquid are  $V_*$  and  $V$  respectively, we get

$$V = V_* e^{\alpha(T-T_*)} \quad \dots (iv)$$

whence by equation (i)

$$\phi = C(V - V_*) = C.V_* \{ e^{\alpha(T-T_*)} - 1 \} \quad \dots (v)$$

$$\text{or,} \quad e^{\alpha T} + \frac{e^{\alpha T_*}}{C.V_*} \phi = e^{\alpha T}$$

$$\text{or,} \quad a + b.\phi = e^{\alpha T} \quad \dots (vi)$$

$$\text{where} \quad a = e^{\alpha T_*} \quad \text{and} \quad b = \frac{e^{\alpha T_*}}{C.V_*}$$

This gives a linear relationship between  $\phi$  and  $e^{\alpha T}$ . It should be mentioned in this connection that in the above derivation the constancy of  $\alpha$  implicitly assumes a constancy of the molecular species which does not change with change of temperature. As to the temperature  $T_*$ , the implication is that at this point the molecules are at their closest approach so that the free volume is the least at this point and the translatory energy is at its minimum.

#### EXPERIMENTAL

About sixty different liquids were examined for their viscosity and coefficient of expansion. More than a dozen (13) cases were locally examined, while the data for the rest were taken from Landolt-Bornstein Tabellen and from the data published under Project No. 44 of the American Petroleum Institute under the National Bureau of Standards, U.S.A.

The liquids locally investigated were of B.D.H. AnalaR quality, distilled twice or thrice till the constancy of the boiling point at their respective standard values was realised. Viscosity was measured relatively to water with the help of an Ostwald viscometer whose average time of flow for water at 30° was observed to be about 30 seconds. These relative values were then converted into centipoise from the absolute viscosity of water as given in the Landolt-Bornstein Tabellen. Reciprocals of these values yielded their fluidities.

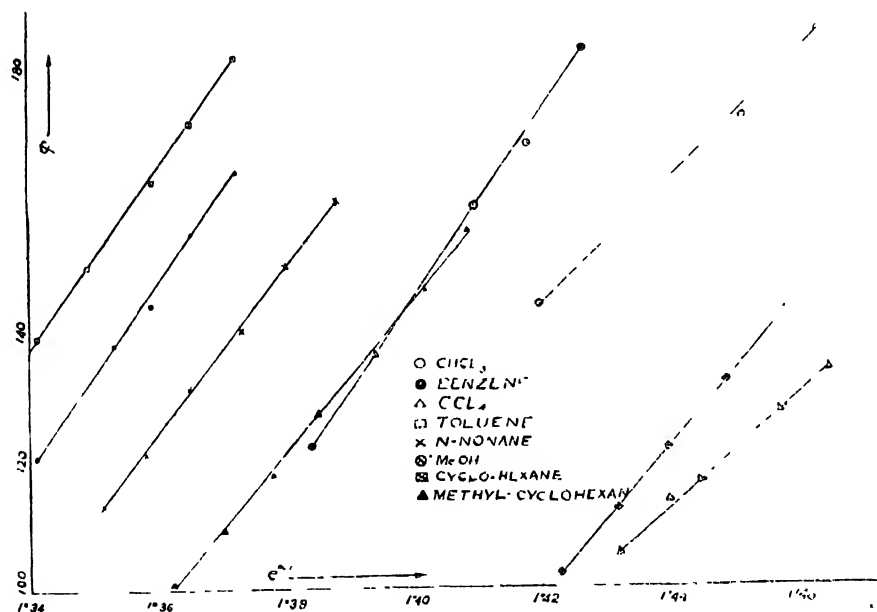
The coefficients of expansion were determined between  $30^{\circ}$  and  $35^{\circ}$  by determination of their densities at these temperatures. The coefficient of expansion for water was ascertained from its densities at  $30^{\circ}$  and  $32^{\circ}$ .

The equation (vi) has been verified within a temperature range of  $0^{\circ}$  to  $40^{\circ}$  with an average value of  $\gamma$  in the range assumed to be constant. For those liquids whose data were taken from the literature cited above, the temperature range has been extended or curtailed according to the availability of the relevant data

## DISCUSSION

*The Linear Relationship.*—The plots of  $\phi$  against  $a''$  are straight lines as expected from equation (vi) with an intercept on the  $a''$ -axis ( $a = e^{T_s}$ ). Some of the cases worked out here have been graphically presented in Fig. 1. From these graphs the values of  $T_s$  were calculated and they were in all cases found to be lower than the

FIG. 1

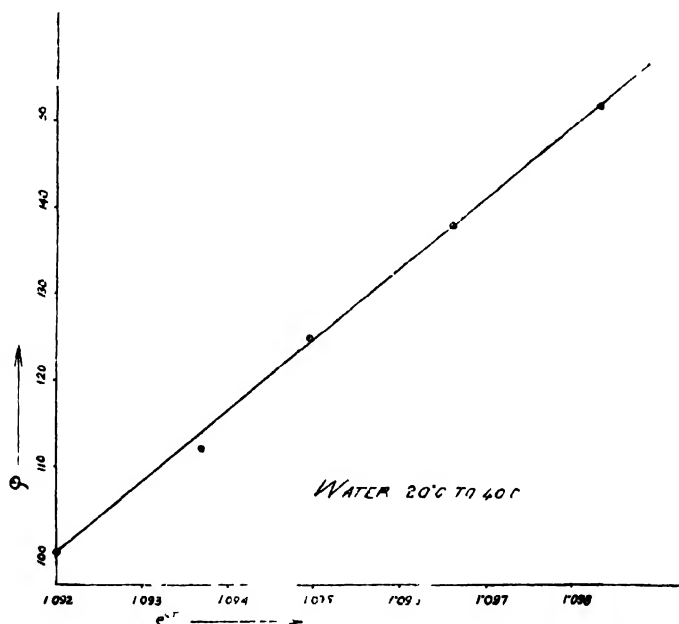


corresponding melting points under atmospheric pressure, excepting in the case of water and acetone, where they were found to be much above their melting temperatures. This fact is significant because the volume  $V_s$  of the liquid at temperature  $T_s$  has been assumed to contain no holes and hence the densities at this temperature ought to be maximum. In the case of water, it is well known that the maximum density is reached at  $4^{\circ}$  under atmospheric pressure, while extrapolation from the present curve for water gives a value of  $T_s$  equal to  $14^{\circ}$ . This discrepancy might be attributed to the fact that the extrapolation has in this case been actually performed on the data for coefficient of viscosity observed between  $20^{\circ}$  and  $40^{\circ}$ . This temperature of maximum density should be best compared with that obtained by extrapolation of the density-temperature curve

for water, specially of the region between  $20^{\circ}$  and  $40^{\circ}$ . Such an extrapolation has been actually carried out on the density-temperature curve given in the Landolt-Bornstein Tabellen (Eg. IIIa, 53) which yielded a value of  $13^{\circ}$  as the temperature of maximum density. The agreement is therefore satisfactory.

Another important feature to be noticed in the case of water is that although water is known to be a highly associated liquid, still it gives a linear relationship (vide Fig. 2) according to equation (vi). This evidently suggests that within a range of  $20^{\circ}$  to  $40^{\circ}$  its molecular species does not alter appreciably. Methyl and ethyl alcohols have also been

FIG. 2



found to give straight lines according to this equation within a range of  $-30^{\circ}$  to  $25^{\circ}$  and  $0^{\circ}$  to  $30^{\circ}$  respectively; they are also known to be highly associated liquids. The case of mercury is interesting from this point of view because liquid mercury is known to be composed of monatomic particles and as such they are much simpler than those of most of the liquids known. It is interesting to notice that mercury maintains a strictly linear relationship throughout the major temperature range over which it remains in the liquid state under atmospheric pressure. The  $T_*$  calculated for mercury comes out to be  $18^{\circ}\text{K}$  ( $= -255^{\circ}\text{C}$ ) which is much below its melting point ( $-39^{\circ}$ ).

**Significance of  $V_*$ .**—As already referred to,  $V_*$  is the volume which the liquid will occupy at the hypothetical temperature  $T_*$ , where its fluidity totally disappears. On the assumption of a proportionality between  $\phi$  and the free volume in a liquid, according to Batschinski's equation, the volume  $V_*$  at  $T_*$  should not have any free volume and the molecules will be packed together in the closest possible orientation. Even at this volume the

free space will not entirely disappear because at the closest packing of spherical molecules there will be gaps in between, though such space may be very small.

It will not be irrelevant to refer here to the superior advantages for using this  $V_s$  for calculation of molecular dimensions over the method based upon the law of rectilinear diameter of Callitot and Mathius (cf. Moelwyn Hughes, *loc. cit.*, p. 30) which rests upon an assumed validity of extrapolation of the mean density over as large a temperature range as from 0°K to the critical temperature of the liquid. The values of molecular radii calculated from  $V_s$  have been given in Table I and compared with those obtained from viscosity of gases and also from Van der Waals' 'b'.

TABLE I

Liquid,	† $r$ calculated from		
	Equ. (vi).	Viscosity.	'b'.
Mercury	1.778 $\text{\AA}$	1.80 $\text{\AA}$	1.79 $\text{\AA}$
Acetone	1.70	1.90	—
Benzene	3.098	2.95	1.07
CCl <sub>4</sub>	2.22	2.38*	1.096
n-Pentane	2.32	2.25	1.14
Ether	3.40	3.10	1.10
Chloroform	2.13	2.14	—

\*The value of  $r$  for CCl<sub>4</sub> in this case has been taken from polarisation data (Moelwyn Hughes, "Introduction to Physical Chemistry", 1940, p. 105).

† $r$ 's denote the molecular radii calculated on the assumption of spherical molecules and  $r$ 's in column 3 signify the radii calculated from the viscosity of these substances in the gaseous state and taken from Landolt-Bornstein Tabellen (Bd. III 5 Aufl., p. 105).

(Obviously the values of  $r$  calculated from  $V_s$  are in general larger than those obtained from Van der Waals' 'b', but show satisfactory agreement so far as the data from viscosity of gases are concerned.

Encouraged by these results the chain lengths of some normal paraffins were also calculated by first ascertaining their molecular volumes from  $V_s$  and dividing this by 21 sq.  $\text{\AA}$ ., the cross-section of these hydrocarbon chains, as determined by the surface film method (vide Glasstone, "Recent Advances in Physical Chemistry", 1933, 2nd Edition, p. 332). The area of cross-section as measured by the film method has been preferred in this case because in a surface film under limiting conditions the molecules are assumed to be in closest packing, as has been pictured in the conception of  $V_s$ . The values appear in Table II below and have been compared with those calculated with the help Mark's formula ("Physical Chemistry of High Polymeric Systems", Part III, 1940, p. 141):  $l = 1.26n + 1.83$ , where  $n$  denotes the number of carbon atoms in the chain and  $l$ , the chain length in  $\text{\AA}$ .

TABLE II

Hydrocarbon.	$l$ calc. from Eqn. (14)	$l$ calc. by Mark's Eqn.	Hydrocarbon.	$l$ calc. from Eqn. (14)	$l$ calc. by Mark's Eqn.
<i>n</i> -Pentane	7.6 Å	8.13 Å	<i>n</i> -Undecane	15.51 Å	15.69 Å
<i>n</i> -Hexane	8.98	9.39	<i>n</i> -Dodecane	16.87	16.95
<i>n</i> -Heptane	10.25	10.65	<i>n</i> -Tridecane	18.90	18.63
<i>n</i> -Octane	11.7	11.9	<i>n</i> -Tetradecane	19.62	19.47
<i>n</i> -Nonane	12.8	13.17	<i>n</i> -Pentadecane	20.9	20.73
<i>n</i> -Decane	14.08	14.43			

The values of  $l$  are in excellent agreement. The equation (vi) can therefore be regarded as a suitable method for computing the dimensions of molecules. The only experimental data that we require for this purpose comprise viscosity and density at least at two different temperatures from which by linear extrapolation the value of  $V_s^*$  is obtained. The assumption of an approximate constancy of the values of  $\alpha$ , on which the present calculations are all based, appears to be justified by the close agreement of the data presented in the above tables.

**Significance of  $T_s$ .**—The concept of  $T_s$ , as already referred to, becomes also of an hypothetical nature where the liquid loses its free space as envisaged by the viscous properties of liquids. If  $V_s$  be regarded as the volume of the solid obtained from the liquid state in which the molecules are in the closest possible packing,  $T_s$  may be looked upon as analogous to the critical temperature between the solid and the liquid states, as their specific volumes at this temperature are equal. It is, however, highly improbable that there would be any relationship between  $T_s$  and  $T_c$ , the gas-liquid critical temperature, because the constancy of  $\alpha$  is not maintained near the critical temperature beyond which the value of  $\alpha$  is known to be as high as 1/273.16 which is the accepted value of  $\alpha$  for gases. Extrapolation of  $T_s$  from  $T_c$  does not therefore appear to be justified.

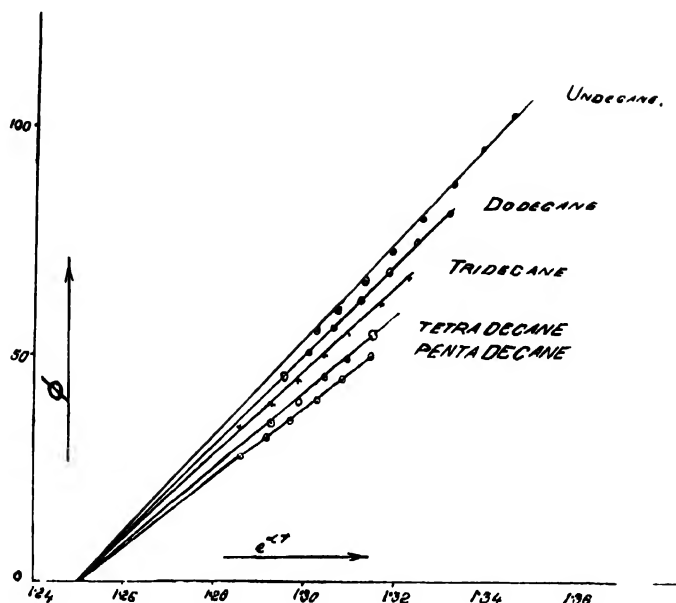
An interesting feature in the  $\phi - e^{aT}$  plots is that the straight lines obtained for the members of the same homologous series have been found to intersect the  $e^{aT}$ -axis at approximately the same point. Five different homologous series have been studied in this connection, two of which have been shown in Figs. 3 and 4. The values of the intercepts are presented in Table III.

TABLE III

Homologous series	$e^{aT_s}$	No. of C atoms where $T_s$ becomes const.
Normal paraffins	1.250	> 21
cycloPentanes	1.252	21
cycloHexanes	1.252	19
Benzene homologues	1.236	19
Normal mercaptans	1.262	—

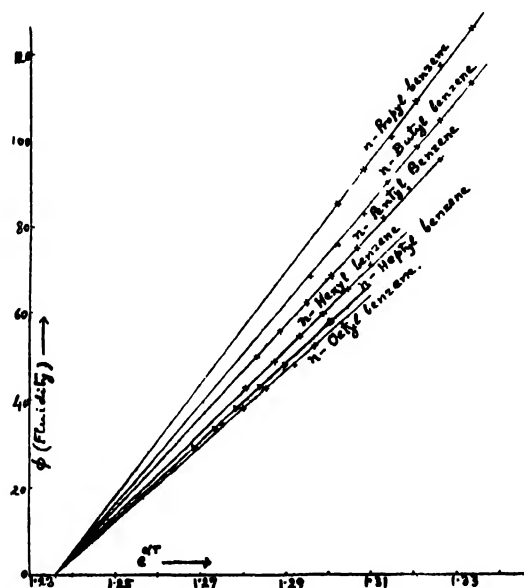


FIG. 3



The three aliphatic homologous series viz., *n*-paraffins, cyclopentanes and cyclohexane homologues have identical values for their intercepts, while that of benzene homologues have slightly lower and the normal alkyl mercaptans, a slightly higher value.

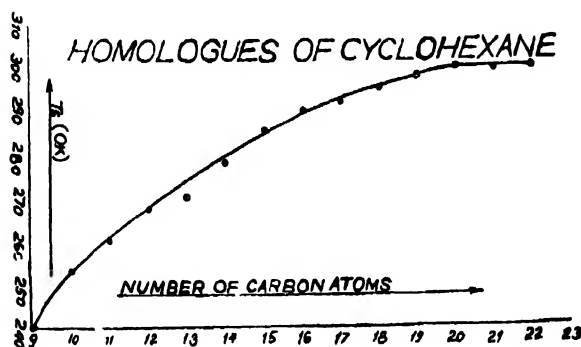
FIG. 4



These observations are interesting in as much as they indicate constancy of  $\phi^{aT}$  for a homologous series which again indicates that  $\alpha T_s$  should be constant. The values of  $T_s$ , 6-1731P-10.

have been calculated for the different series and have been observed to change with the number of carbon atoms in the chain in the typical manner as shown for the different series studied herein (Fig. 5). The number of carbon atoms at which the curve shows a tendency to reach a constant value have been shown in column 3 of Table III. The constancy of the product  $\alpha T_n$  and the manner of variation of  $T_n$  with the number of carbon atoms in the chain are suggestive that  $T_n$  might be a fundamental and charac-

FIG. 5



teristic quantity for a definite homologous series. Further work is necessary for elucidation of this aspect which is in progress and will be reported in a future communication.

The author's best thanks are due to Prof. S. N. Mukherjee, D.Sc. for suggesting this problem and also to Prof. H. L. Roy, Dr. Ing. and to the authorities of the Institution for giving me every facility in their library and laboratories.

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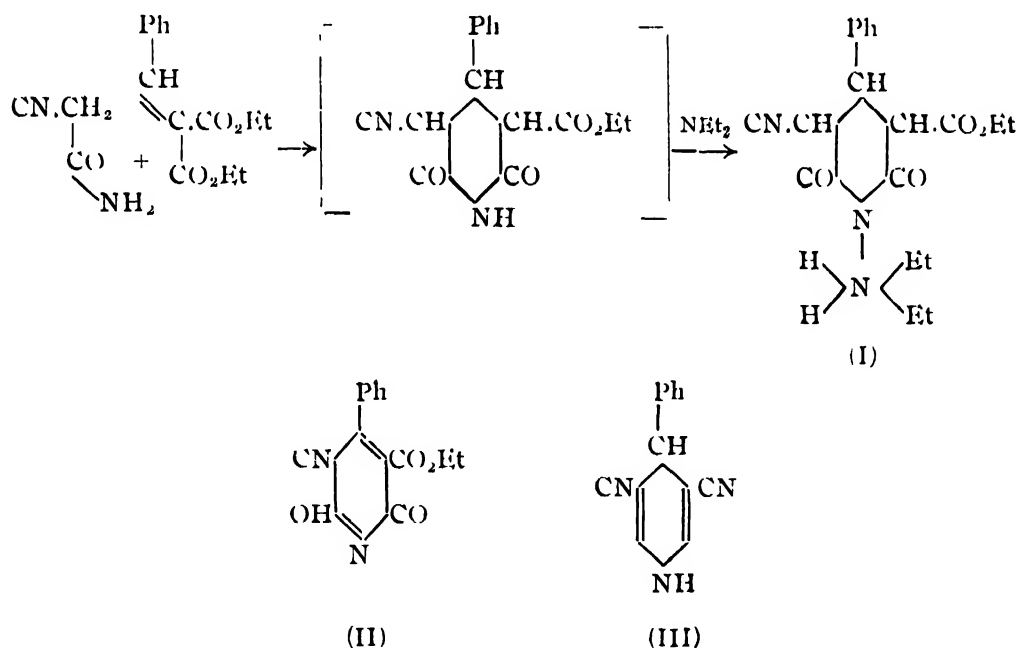
Received May 25, 1949

# A MODIFICATION OF THE GUARESCHI PYRIDINE SYNTHESIS. PART III

By NIRMALANANDA PALIT

Synthesis of certain pyridine derivatives by the reaction of benzylidene-esters and-ketones with cyanoacetamide and aminoacrylonitriles are described.

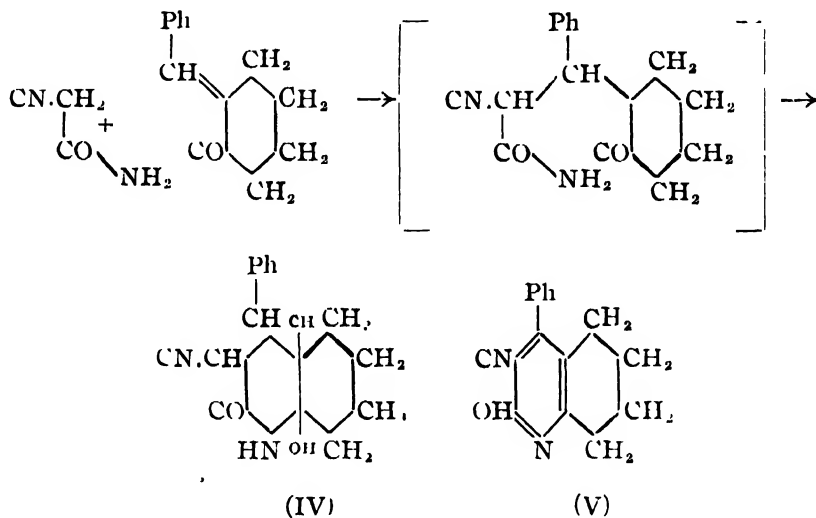
In the earlier communications it has been shown that cyanoacetamide and  $\beta$  amino- $\beta$ -arylacrylonitriles react with benzylidene-acetoacetic ester and benzylidene-cyanoacetic ester to give various pyridine derivatives (this *Journal*, 1937, 14, 219, 354). The reaction has now been extended to benzylidene-malonic ester and benzylidene-cyclohexanone with similar results. With diethylamine as the condensing agent, the former reacted with cyanoacetamide to give a diethylammonium salt of diketopiperidine (I), while if sodium ethoxide was used, the normal dihydro-oxyppyridine (II) resulted.



(I) is easily transformed into (II) by heating for a few minutes with dilute HCl, whereas hot caustic soda opens up the pyridine ring with the formation of diethylamine and ammonia.

The aminoacrylonitriles were much less reactive, diethylamine having failed to bring about the reaction. With sodium ethoxide, the molecule decomposed liberating benzaldehyde which reacted with two molecules of the acrylonitrile to give (III), described previously by Meyer (*Chem. Zentr.*, 1908, II, 591). The reaction was more fruitful with Kohler and Souther's reagent (few drops of sodium methoxide in absolute methyl alcohol, *J. Amer. Chem. Soc.*, 1922, 44, 2903).

With benzylidene-cyclohexanone, if diethylamine was used as the condensing agent, cyanoacetamide added at the double bond and the additive product suffered ring-closure by tautomerisation between the 1:6-positions to give (IV), as observed previously (cf. Sen Gupta, *J. Chem. Soc.*, 1915, 107, 1347). Sodium ethoxide gave the normal tetrahydroquinoline derivative (V).



#### EXPERIMENTAL

##### Reactions of Ethyl Benzylidene-malonate

(a) *With Cyanoacetamide:* (i) *Formation of Diethylammonium Salt of 3-Carbethoxy-5-cyano-2:6-diketo-4-phenylpiperidine.*—The amide (0.8 g.) suspended in the unsaturated ester (2.5 g.) was treated with diethylamine. Next day it set to a solid mass. After three days, some alcohol was poured in, solids crushed and dissolved by heating and some fresh amine added. Next day the crystalline deposit was filtered and washed. It shrinks at  $175^\circ$  and melts with decomposition and evolution of gas at  $180^\circ$ . It is soluble in hot water and it readily dissolves in  $\text{NaOH}$ . The latter evolves diethylamine on warming. An alcoholic solution on exposure to air develops a deep violet tint. It was recrystallised from alcohol, m.p.  $183^\circ$  (decomp.), yield 2.8 g. (Found: C, 63.69; H, 6.92; N, 12.02.  $\text{C}_{10}\text{H}_{12}\text{O}_4\text{N}_2$  requires C, 63.51; H, 6.96; N, 11.70 per cent).

(ii) *Formation of 5-Cyano-3-carbethoxy-6-hydroxy-4-phenyl- $\Delta^{3,6}$ -dihydro-2-pyridone.*—The amide was added to sodium ethoxide solution and well shaken. To the suspension of sodiocyanoacetamide the ester was added. On shaking the white colour rapidly changed to yellow, then to flesh colour and finally to violet. The mixture got warmed up and in a few minutes the whole thing set to a violet mass. Next day the solid was no longer violet but pale yellow sodium derivative of the oxypyridine, but the surface layer and the surface of the container above it were deep violet, the colour deepening still more as soon as the stopper was opened and exposed to air. On adding water the solid dissolved. Acidification produced a heavy oil which solidified

on standing in ice. These were filtered and twice crystallised from alcohol as elongated plates (under the microscope), m.p.  $179^{\circ}$ . (Found: C, 63.0; H, 4.55; N, 10.1.  $C_{15}H_{12}O_4N_2$  requires C, 63.39; H, 4.23; N, 9.85 per cent).

(b) *With  $\beta$ -Amino-p-anisylacrylonitrile: Formation of 5-Cyano-3-carbethoxy-4-phenyl-6-anisyl-2-oxypyridine.*—Molecular quantities of the reactants were dissolved in absolute methyl alcohol and two drops of a solution of sodium methoxide in methyl alcohol added. It was allowed to stand for two weeks, boiled under reflux for four hours and again allowed to stand. A shining white, wooly, crystalline mass separated. It is insoluble in sodium carbonate but soluble in caustic soda from which acids reprecipitate it. It was recrystallised from methyl alcohol, m.p.  $204^{\circ}$ . (Found: N, 7.82.  $C_{22}H_{18}O_4N_2$  requires N, 7.5 per cent).

(c) *With  $\beta$ -Amino-p-tolylacrylonitrile.*—As above, the mixture was allowed to stand for two weeks, boiled and again allowed to stand. It was recrystallised from methyl alcohol in mesh of needles, m.p.  $208^{\circ}$ . (Found: N, 8.2.  $C_{22}H_{18}O_3N_2$  requires N, 7.82 per cent).

#### *Reactions of Benzylidene-cyclohexanone*

(a) *With Cyanoacetamide: (i) Formation of 9-Hydroxy-3-cyano-4-phenyldecahydro-2-quinolone.*—The ketone was added to a hot alcoholic solution of the amide and diethylamine added. The mixture was kept warm for 3 hours. The colour very gradually deepened from yellow to yellowish brown. Next day a small amount of crystals deposited at the bottom (m.p.  $156^{\circ}$ ) which dissolved in water and caustic soda and evolved ammonia on warming with the latter suggesting it to be an open-chain addition product. After a few days the solution showed a strong yellow-green fluorescence. The solvent was evaporated off and the residual gummy mass was crystallised from ethyl acetate as hard nodules, m.p.  $265-68^{\circ}$  with shrinking and turning brown. It is insoluble in hot water but soluble in hot NaOH from which HCl regenerates it. It was recrystallised from alcohol in light, pointed, microscopic lancets, m.p.  $272^{\circ}$ . (Found: N, 10.66.  $C_{16}H_{18}O_2N_2$  requires N, 10.37 per cent).

(ii) *Formation of 3-Cyano-2-oxo-4-phenyl-ar-tetrahydroquinoline.*—Sodium (0.23 g.) was used in absolute alcoholic solution with molecular quantities of the reactants. Colour gradually changed and fluorescence developed. The solvent was evaporated off and the sticky residue rubbed with water and allowed to stand overnight. The white solid so obtained (2 g.) was crystallised from a large volume of alcohol, m.p.  $257-58^{\circ}$ . (Found: N, 11.42.  $C_{16}H_{11}ON_2$  requires N, 11.20 per cent).

(b) *With  $\beta$ -Amino-p-tolylacrylonitrile: Formation of 3-Cyano-4-phenyl-5-tolyl-ar-tetrahydroquinoline.*—It was prepared as above. After standing for a week the solid deposited was collected and washed with hot water and crystallised from alcohol in yellow nodules, m.p.  $196^{\circ}$ . (Found: N, 8.81.  $C_{23}H_{20}N_2$  requires N, 8.64 per cent).

## REVIEWS

**Absorption Spectrophotometry.**—By G. F. Lothian. Published by Hilger and Watts Ltd., London, 1949. Pp. 196 + 6 plates. Price 26 sh. net.

This book is primarily intended for supplying useful information to research workers interested in quantitative analysis of organic compounds by spectrophotometric methods. In the first five chapters the principles of spectrophotometry have been explained elaborately indicating finally how quantitative analysis is made from the absorption spectrograms. In the next three chapters various applications of spectrophotometry including detection of certain groups of atoms in molecules, metallurgical analysis, estimation of hydrocarbons and other biological and biochemical applications have been described. The last four chapters are devoted to detailed description of the technique used in spectrophotometry. Different types of spectrophotometers with their accessories have been described in detail and their performances have also been shown with the help of beautiful illustrations. There is a fairly exhaustive bibliography at the end.

The book will be found to be very useful to post-graduate research workers engaged in this line of research, because they will get in it information not only regarding the fundamental principles involved but also regarding the methods in which different types of spectrophotometers available in the market can be employed.

S. C. S.

**Gmelins Handbuch der Anorganischen Chemie.** Achte Auflage. Selen B. with 11 figures : Systemnumber 10, 1949. Pp. 195 + xxi + vii. Clausthal-Zellerfeld, Gmelin-Verlag G. m. b. H.

The present volume constitutes the part B of the System Number 10 – Selenium, of the fully revised 8th Edition of the well-known treatise, Gmelin's Handbook of Inorganic Chemistry. The book deals with the compounds of Selenium. Gmelin's Handbook is too well-known to require any detailed review ; no research laboratory can afford to do without it. The present volume has fully maintained the reputation of its predecessors. References to original works up to 1948 have been incorporated in the book.

P. R.

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and the diagrams are neat and fully illustrative. The book is sure to prove useful to scientific workers, as temperature control is very necessary in many industrial operations and accurate experimental work on physico-chemical problems.

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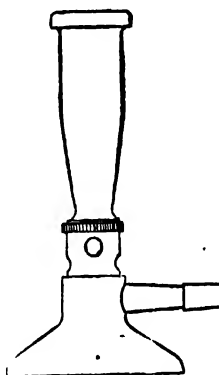
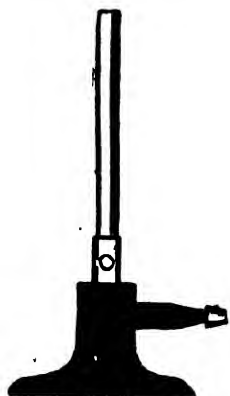
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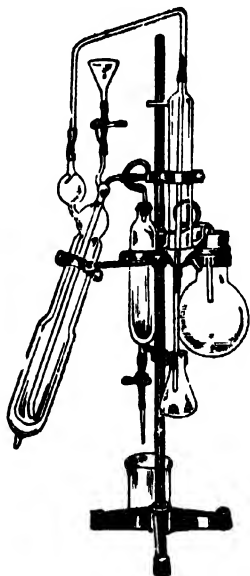
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# PRODUCTION OF THE JOSHI EFFECT IN OXYGEN UNDER SILENT ELECTRIC DISCHARGE. PART V. INFLUENCE OF THE FREQUENCY OF THE EXCITING POTENTIAL

By S. R. MOHANTY

Influence of the frequency  $f$  of the exciting potential on the Joshi effect  $\Delta i$  in oxygen, enclosed in a Siemens' tube at 331 mm. ( $32^\circ$ ) Hg pressure, has been investigated. Both the 'threshold' potential  $V_m$  and  $\Delta i$  decrease, the former from 2.7 to 0.7 kV (r. m. s.) and the latter from 42 to 21 % (current  $i$  in dark,  $i_0 = 3$ ), with  $f$  increased from 50 to 500  $\omega$ .  $\Delta i$  is negligibly small below  $V_m$ . It is absent in high frequency (3-11 M $\omega$ ) conduction at low potentials. Since the proportion of dielectric in  $i$  increases with  $f$ , and conduction mainly dielectric below  $V_m$  and with high frequencies at low potentials, the above results do not support Parshad's view that  $\Delta i$  represents a diminution of the dielectric as distinct from conduction current. Diminution of wattage dissipated in the ozoniser on irradiation corresponding to  $\Delta i$  indicates on the other hand that  $\Delta i$  results chiefly from suppression of conduction current. Change under light of dielectric conductivity can, at best, be a minor explanation.

It has already been shown (Part I, Mohanty and Kamath, this *Journal*, 1948, 26, 405; Mohanty, Part VI, *ibid.*, communicated) that the magnitude of the Joshi effect  $\Delta i$  in oxygen is dependent upon the applied (alternating) potential  $V$ . That the frequency  $f$  of this last is another important determinant, was revealed by the preliminary investigations of the author (*Proc. Indian Sci. Cong.*, 1949, Part III, *Chem. Sec.*, Abst. No. 25). It was of interest therefore to study this in some detail.

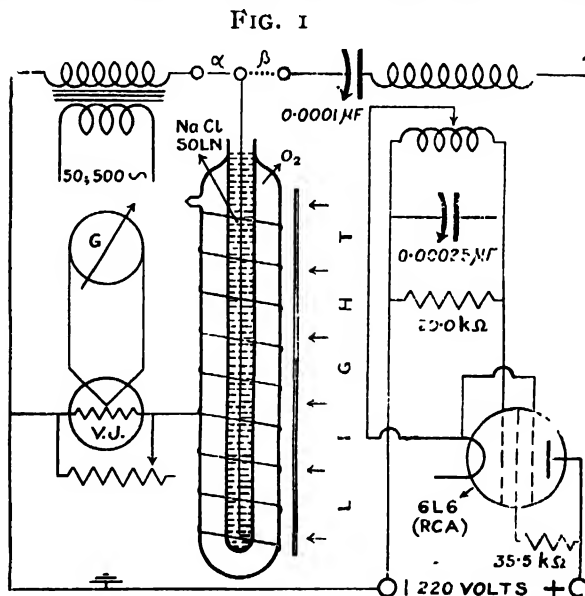
## EXPERIMENTAL

Single phase alternating currents of 50 and 500 cycles frequency were obtained from rotary converters worked off 220 volts, D. C. mains. A Hartley type oscillator was used for generating high frequencies.

The general experimental arrangement and the circuit employed are shown in Fig. 1. The oscillator consisted chiefly of a 6L6 pentode (RCA), 20,000 $\Omega$  grid resistance, 0.00025  $\mu$ F tuning condenser and tuning inductance. A variable 0.0001  $\mu$ F capacitance was included in series with the receiving coil; this served to tune the receiving circuit to the frequencies generated by the oscillator. The frequency  $f$  was varied by altering the dial-position, and hence the capacitance of the tuning condenser. From calibrations made with a wavemeter,

the various dial-positions corresponded to the frequency range of 3-11 megacycles per second.

A Siemens' tube filled with purified oxygen at 331 mm. pressure ( $32^\circ$ ) served as the discharge vessel. The current was observed with a reflection galvanometer G, actuated by a Cambridge vacuo-junction V. J. (Fig. 1). The source of light consisted



of a battery of two 200 watt incandescent (glass) bulbs run at 200 volts, and placed at a distance of 20 cm. from the discharge tube. The mode of observation of  $\Delta i$  was similar to that described in Part I (Mohanty and Kamath, *loc. cit.*).

Three series of observations were made: (i) when the discharge tube was excited at different  $V$  varied in the range of 2-6 kV (r. m. s.) of 50 cycles frequency, (ii) with 0.5-1 kV of 500 cycles frequency, and (iii) when the system was fed with high frequencies in the aforementioned range. The potential developed across the ozoniser in (iii) was kept constant; it was, as determined with a thermionic tube voltmeter, 1.17 volts. The relevant circuit for (i) and (ii) is represented by  $\alpha$ , and that for (iii) by  $\beta$  (Fig. 1). The current in dark  $i_n$ , that under irradiation  $i_L$ , the net Joshi effect  $\Delta i$  and the relative effect  $\% \Delta i$  for different  $V$  and  $f$  are given in Table I.

TABLE I

*Influence of the frequency of exciting potential on the Joshi effect in oxygen.*

$pO_2 = 331$  mm. ( $32^\circ$ ).

Temp. =  $20^\circ$ .

Detector = Vacuo-junction.

Source of radiations = Two 200 volt-200 watt (glass) bulbs, 20 cm. from the ozoniser.

V (kV, r. m. s.)	$i_n$	$i_L$	$\Delta i$	$\% \Delta i$
50 $\sim$ ; $V_m = 2.7$ kV (r. m. s.)				
2.4	1	1	—	—
2.67	2.55	1.41	1.14	44.7
2.93	5.48	3.46	2.02	36.9
3.2	7.62	5.2	2.42	31.8
3.47	8.94	6.65	2.38	26.6
3.73	10.10	7.55	2.55	25.2
4	11.14	8.49	2.65	23.8
4.27	12.13	9.27	2.86	23.6
4.53	13.15	10.20	2.95	22.4
4.8	14.21	11.09	3.12	22
5.07	15.30	11.96	3.34	21.8
5.33	16.25	13.00	3.25	20.0
500 $\sim$ ; $V_m = 0.7$ kV (r. m. s.)				
0.67	—	—	—	—
0.69	2.65	2.12	0.53	20.0
0.72	4.60	3.74	0.95	20.3
0.75	7.55	6.00	1.55	20.5
0.77	10.20	8.49	1.71	16.8
0.8	12.84	10.73	2.11	16.4
0.83	16.19	13.93	2.26	14
0.85	20.04	17.41	2.63	13.1
3-11 M $\sim$ .				
Dial position of condenser.	Approx. $f$ in M $\sim$ .			
0	3.4	9.5	9.5	—
30	3.7	7.6	7.6	—
60	4.0	15.6	15.6	—
90	4.5	15	15	—
120	5.3	10.6	10.6	—
150	6.7	10.7	10.7	—
180	10.6	12.4	12.4	—

## DISCUSSION

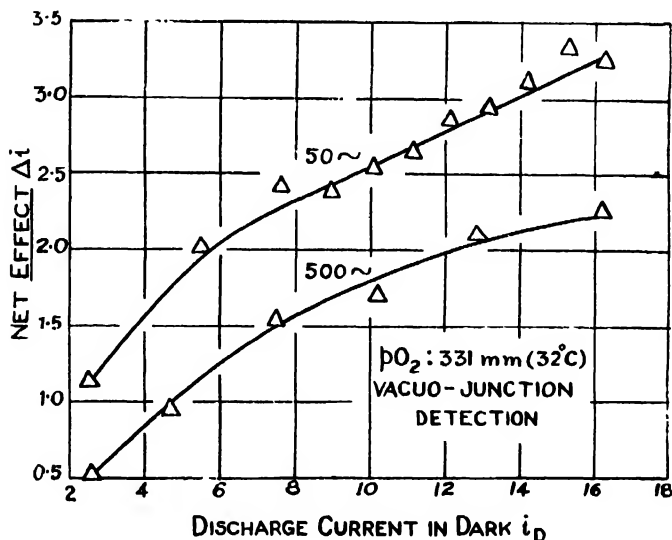
It has been shown by Joshi (*Curr. Sci.*, 1939, **8**, 548) that measurements of the minimum 'threshold' potential  $V_m$ , at which  $i$  increases rapidly with the applied  $V$ , are markedly sensitive to changes in  $f$ . That  $V_m$  would appear to be more sensitive to such changes than the Paschen potential has also been emphasized by him (Joshi, *ibid.*, 1946, **15**, 281). In agreement with the above, it is observed that whereas  $V_m$  for 50 cycles is about 2.7 kV, it is as small as 0.7 kV, under otherwise identical conditions, with 500 cycles (cf. Table I). Further, increase of  $i$  with  $V$  is far more rapid in the latter than in the former case. Thus *e.g.*, increase of  $V_{f=50}$  from 2.67 to 5.33 kV increases  $i_b$  from 2.55 to 16.25 units, *i.e.*, by about 6 times; the corresponding  $i_L$  increases by about 9 times, from 1.41 to 13.00. On the other hand, increase of  $V_{f=500}$  over a comparatively small range, *viz.*, from 0.69 to 0.85 kV, increases  $i_b$  from 2.65 to 20.04 *i.e.*, by about 7 times;  $i_L$  increases by about 8 times, from 2.12 to 17.41, over the same potential range.

In agreement with the general result due to Joshi (*Proc. Ind. Acad. Sci.*, 1945, **A22**, 389), and the earlier observation of the author and Kamath (*loc. cit.*) in the gas, it is found that the effect is not observed below  $V_m$ . Further,  $\% \Delta i$  is maximum near this potential; it is 44.7 with 50 cycles, and 20.0 with 500 cycles. These results bring out the fundamental significance of  $V_m$  in relation to the Joshi effect phenomenon.

Since the exciting potentials were, of necessity, different in the two cases, it is not possible to compare  $\Delta i$  or  $\% \Delta i$  at 50 and 500 cycles under conditions of constant  $V$ . Comparisons are therefore made under conditions of constant  $i_b$ . For this purpose, values for  $\Delta i$  at the above two frequencies are plotted against the corresponding values of  $i_b$  (Fig. 2). It will be seen that the curve for 500 cycles is well below that for 50 cycles, indicating that under constant  $i_b$  conditions,  $\Delta i$  for 50 cycles is larger than that for 500 cycles. This supports the general validity of Joshi's observation (*Proc. Ind. Acad. Sci.*, 1945, **A22**, 389) that *ceteris paribus*  $\% \Delta i$  decreases as the input frequency (*i.e.*, of the A. C. supply) is increased.

Results in Table I reveal further that the system excited with high frequencies in the range 3-11 megacycles does not show the effect. The observations of Joshi and Lad (*ibid.*, 1945, **A22**, 293), Tiwari and Prasad (*Curr. Sci.*, 1945, **14**, 229), Lahiry and Das-Gupta (*Proc. Ind. Sci. Cong.*, 1949, Part III, *Phys. Sec.*, Abst. No. 30), and Das-Gupta (*Science & Culture*, 1945-46, **11**, 318) with chlorine were similar. The chief determinant of the Joshi effect phenomenon is a large enough field to produce ionisa-

FIG. 2



tion by collision of the gas in the annular space. The *effect* is absent under high frequency conduction, since under such conditions the corresponding electric field is so low that the system functions as a capacity only.

Parshad (*Nature*, 1945, 155, 362) has envisaged the mechanism of the Joshi effect from the standpoint of Kramers' quantum mechanical theory of light dispersion. He considers that consequent on irradiation, the gas is excited to higher vibrational and electronic states. For these, due to operations of negative terms in Kramers' dispersion formula, the refractive index  $n$  should be less than that of the normal gas. It follows from this, and the well-known relation due to Maxwell, viz.,  $n^2 = \epsilon$  (where  $\epsilon$  is the dielectric constant) that  $\epsilon$  should diminish. Since this last is a measure of the electrostatic capacity of the system, Parshad concludes that the Joshi effect represents a diminution of the displacement, as distinct from conduction or ohmic, current. Since ionisation and excitation are different stages in the same direction, the smaller dielectric constant of ionised as compared with unionised gases constitutes, according to him, an indirect experimental confirmation of the above interpretation. The results of the present experiments, however, do not support Parshad's view. Thus, whereas  $\Delta i$  decreases with  $f$ , the proportion of the dielectric current is known to increase. Further,  $\Delta i$  is negligibly small below  $V_m$  (at which ionisation by collision commences in the annular space), and does not occur with high frequencies at low potentials; conduction in both these cases is mainly capacitative. From the observation that the wattage dissipated in the ozoniser decreases on irradiation corresponding to  $\Delta i$ , Joshi (*Proc. Ind. Acad. Sci.*, 1945, A22, 225) concludes that the *effect*  $\Delta i$  results chiefly from a reduction of the conduction or ohmic part of  $i$ . Further, he observes, "that the corresponding displacement current may also be affected is suggested by a frequent observation of a sensible movement and distortion on irradiation of the steadied wave-form on the oscillograph, due perhaps to a frequency or/and phase shift; by the observed influence on % $\Delta i$  of capacitative changes in the system, suggesting a change under light of the dielectric constant of the ionised gas as a possibly partial, though at best a minor explanation of this phenomenon of ageing, adsorption and the nature of the wall material".

Grateful thanks of the author are due to Professor S. S. Joshi for having suggested the problem and for his keen interest in the work, and to Mr. P. L. Sarma for having kindly constructed the H. F. generator.

DEPARTMENT OF CHEMISTRY,  
BENARES HINDU UNIVERSITY.

Received July 12, 1949.

## PHENYL- $\alpha$ -NAPHTHYLAMINE-AZOBENZENE *p*-SULPHONIC ACID AS ADSORPTION INDICATOR

BY RAM CHARAN MEHROTRA

A new adsorption indicator, phenyl- $\alpha$ -naphthylamine-azobenzene *p*-sulphonic acid has been suggested for argentometric titrations. It differs from all the classical adsorption indicators in having both acidic as well as basic character which makes it applicable both in the titrations of halide ions against silver ions as well as in the reverse titrations of silver ions against halide ions in which acidic and basic dyes respectively used to be employed separately. The adsorbability of the indicator, both by the positively as well as negatively charged silver halide bodies, endows it with a sharp colour change at the end-point, a ready reversibility and a large range of applicability in the argentometric titrations.

In a recent communication from these laboratories (Mehrotra, *Anal. Chim. Acta*, 1948, 2, 36), the author has described the applicability of congo red as adsorption indicator in argentometric titrations. This indicator essentially differs from all other previously described adsorption indicators, because it combines within itself the properties of the acidic dyestuffs like phthaleins and basic dyes like rhodamines, and hence can be used in both the titrations in which the above classes of dyes have been separately employed. The present communication extends the study to another dye of the same type, viz., phenyl- $\alpha$ -naphthylamine-azobenzene *p*-sulphonic acid.

Phenyl- $\alpha$ -naphthylamine-azobenzene *p*-sulphonic acid exhibits a marked colour change from violet to red-orange in the  $p_H$  range of 3 to 5. On account of the presence of the acid sulpho group in the molecule, it was expected that the positively charged silver halide particles would adsorb the red-orange anions of the dye, but the negatively charged silver halide body would show a preferential adsorption of the violet cations of the dye. Thus it was expected that the indicator would mark the end-point in the titration of halide ions with silver ions by a colour change from violet-blue to red-orange on the particles, whereas in the reverse titrations, it would show the opposite colour change. However, in the neutral medium ( $p_H$  7), the silver halide particles were found to show an irreversible adsorption for the red-orange anions of the dye, but the red coloured precipitate thus obtained exhibited a colour change which prompted further investigation. On adding a drop of dilute nitric acid to the red particles, they immediately took up a deep blue shade which again changed to red on the addition of a slight excess of ammonia on the particles. Therefore, the titrations were repeated in the  $p_H$  range of 3 to 5, and it was found that in this range, the dye was capable of indicating the end-point with very sharp and reversible colour change both in the titrations of halide ions against silver ions as well as in the reverse titrations of silver ions with halide ions.

### EXPERIMENTAL

A B.D.H. sample of the dye, phenyl- $\alpha$ -naphthylamine-azobenzene *p*-sulphonic acid was recrystallised and its 0.2% solution used as adsorption indicator throughout these investigations.

The potassium chloride, bromide, iodide and thiocyanate and silver nitrate were taken of the B.D.H. AnalaR standard and their standard solutions were prepared by the well known methods.

*Titration of Chloride Ions against Silver Ions and vice versa.*—As stated above, when the titration of potassium chloride (about  $N/10$ ) is carried out with silver nitrate (of about the same strength) with 8 to 10 drops of the indicator for every 10 c.c. of the chloride solution, the pink colour of the suspension does not show any colour change as silver nitrate solution is run in. However, as suggested by Fajans, the dye regulates the beginning of coagulation of the precipitate such that the coagulation of the suspension along with simultaneous adsorption of the dye occurs at the equivalent point. The end-point is quite sharp, but its usefulness is very much limited by its irreversible nature. However, if the  $p_H$  of the medium is regulated between 3 and 5, the coagulation of the precipitate occurs much earlier and the coagulated particles adsorb the dye with the development of blue colour on the particles. Just at the equivalent point, half a drop of the silver nitrate solution in excess turns the blue colour on the coagulated particles into a red shade. The end-point though occurring on the coagulated particles is quite reversible. The reversibility and the sharpness of the colour change can be augmented by the addition of 1 c.c. of 5% chloride-free dextrin solution per 10 c.c. of the chloride solution taken. Dextrin is a protective colloid and does not allow the precipitate to coagulate, and hence the colour change in its presence occurs in the colloidal phase. However, for a sharp colour change to occur, the  $p_H$  of the solution should be carefully controlled in the range of 3 to 5. If the  $p_H$  of the medium becomes too low, say 1 to 2, then the precipitate does not become red at the equivalent point, but remains blue and requires a sufficient (about 4 to 6%) excess of silver nitrate before the particles assume a red shade. On the other hand, if the  $p_H$  of the medium becomes higher than 5, then the blue colour on the particles does not appear and the end-point is similar to the one described in neutral medium.

In the reverse titration of silver ions with chloride ions, the coagulation of the particles occurs much earlier and also the adsorption of the dye with a red shade on the precipitate. As the equivalent point approaches, the red colour on the particles has a tendency to change to blue. Just at the equivalent point, the bluish red colour on the particles changes to a sharp blue with half a drop of the chloride solution. The colour change at the end-point becomes sharper if a few drops of the indicator solution are added again near the end-point. The end-point though occurring on the coagulated particles is very sharp and quite reversible; it can be further improved by the addition of a protective colloid like dextrin. The  $p_H$  of the medium must be within 3 to 5.

*Titration of Bromide Ions against Silver Ions and vice versa.*—In neutral solution, the titration of bromide ions also yields results just similar to those described for chloride ions. In the  $p_H$  range of 3 to 5, the coagulation of the precipitate occurs much earlier and the particles adsorb the dye with the development of a bluish green colour. Just at the equivalent point, half a drop of the silver nitrate solution changes the colour of the precipitate from bluish green to red. The colour change at the end-point is quite reversible and very sharp. The titration can be carried out with sharp end-point even when the titrating solutions have a dilution as low as  $N/200$ ; the coagulation, however, does not occur in the more dilute solutions and the colour change is observed in the apparently homogeneous phase.



In the reverse titration of silver ions against bromide ions, the coagulation occurs much earlier and the particles adsorb the dye with the development of a bright red colour which changes sharply to blue at the equivalent point. Addition of a few drops of the indicator near the equivalent point makes the colour change at the end-point much sharper. In the more dilute solutions of the order of  $N/100$ , the silver bromide does not coagulate out and the colour change occurs in the suspension.

*Titration of Thiocyanate Ions against Silver Ions and vice versa.*—The thiocyanate ions when titrated against silver ions give results similar to those with bromide ions. When the titration of thiocyanate ions against silver ions is carried out in the  $p_n$  range of 3 to 5, colour change from bluish violet to pink occurs at the equivalent point. The titration can be carried out with sharp end-point up to a dilution of  $N/100$ . In the reverse titration, opposite colour change occurs on the coagulated particles.

*Titration of Iodide Ions against Silver Ions and vice versa.*—In the titration of iodide ions against silver ions in the  $p_n$  range of 3 to 5, coagulation occurs much earlier and the particles assume a greenish blue shade. Just at the equivalent point, the colour of the particles changes sharply to red. The colour change at the end-point is very sharp and quite reversible. The end-point remains very sharp even when the titrating solutions are as dilute as  $N/500$ . The reverse titrations of silver ions against iodide ions can be carried out with very sharp end-points indicated by a colour change from red to bluish green.

TABLE I

Vol. & conc. of halide soln.	Indicator (drops).	Vol. & conc. of $\text{AgNO}_3$ soln.	Transition of colour.	Detailed conditions.
$N/10\text{-KCl}$ , 10 c.c.	8	$N/10$ , 9.98 to 10.02 c.c.	Violet pink susp. → pink ppt.	Coagulation just at the end-point with transference of colour from suspension to ppt. End-point is sharp but irreversible.
$N/10\text{-KCl}$ , 10 c.c. + 2 to 4 c.c. of $N/500\text{-HNO}_3$	8	$N/10$ , 10 to 10.02 c.c.	Blue ppt. → pink ppt.	Coagulation occurs much earlier. Colour change occurs on the coagulated particles. The end-point is very sharp and quite reversible. If titration is carried out in presence of a little dextrin, the colour change occurs in the suspension phase.
$N/10\text{-KCNS}$ , 10 c.c. + 2 to 4 c.c. $N/500\text{-HNO}_3$	6	$N/10$ , 10 to 10.02 c.c.	Violet blue ppt. → pink ppt.	Coagulation occurs much earlier. The colour change occurring on the coagulated particles is very sharp and quite reversible.
$N/100\text{-KCNS}$ , 10 c.c. + 2 to 4 c.c. $N/500\text{-HNO}_3$	4	$N/100$ , 10 to 10.04 c.c.	Violet blue susp. → pink susp.	The colour change occurring in the homogeneous suspension phase is quite sharp and reversible.
$N/10\text{-KBr}$ , 10 c.c. + 2 to 4 c.c. $N/500\text{-HNO}_3$	8	$N/10$ , 10 to 10.04 c.c.	Bluish green ppt. → pink ppt.	The colour change though occurring on coagulated particles is very sharp and quite reversible.
$N/100\text{-KBr}$ , 10 c.c. + 2 to 4 c.c. $N/500\text{-HNO}_3$	6	$N/100$ , 10 to 10.04 c.c.	Bluish susp. → pink susp.	Very sharp and reversible end-point occurring in the suspension phase.
$N/10\text{-KI}$ , 10 c.c. + 2 to 4 c.c. $N/500\text{-HNO}_3$	8	$N/10$ , 10 to 10.02 c.c.	Bluish green ppt. → pink ppt.	The end-point is very sharp and quite reversible.
$N/500\text{-KI}$ , 10 c.c. + 2 to 4 c.c. $N/500\text{-HNO}_3$	4	$N/500$ , 10 to 10.02 c.c.	Bluish susp. → pink susp.	The end-point occurs in the suspension phase and is very sharp and quite reversible.

TABLE II

Vol. & conc. of $\text{AgNO}_3$ soln.	Indicator (drops).	Vol. & conc. of halide soln.	Transition of colour.	Detailed conditions.
$N/10\text{-AgNO}_3$ , 10 c.c. + 2 to 5 c.c. of $N/500\text{-HNO}_3$	4	9.98 to 10.02 c.c. of $N/10\text{-KCl}$ or $\text{KCNS}$	Violet ppt. → blue ppt.	The coagulation occurs much earlier and the particles adsorb the dye with a pink shade. As the end-point approaches, the pink colour on the particles changes to violet. Just at the end-point, the particles change their shade from violet to blue. The end-point is very sharp and quite reversible. The colour change is made sharper by the addition of a few drops of the indicator near the end-point.
$N/10\text{-AgNO}_3$ , 10 c.c. + 2 to 5 c.c. of $N/500\text{-HNO}_3$	4	9.98 to 10.02 c.c. of $N/10\text{-KBr}$ or $\text{KI}$	Violet pink ppt. → blue ppt.	Coagulation occurs much before the end-point. The colour change occurring on the coagulated particles is very sharp and quite reversible.
$N/100\text{-AgNO}_3$ , 10 c.c. + 2 to 5 c.c. $N/500\text{-HNO}_3$	4	9.98 to 10.0 c.c. of $N/100\text{-KBr}$	Pink susp. → blue susp.	The colour change occurs in the suspension phase and very sharp and quite reversible.
$N/500\text{-AgNO}_3$ , 10 c.c. + 2 to 5 c.c. $N/500\text{-HNO}_3$	4	9.98 to 10.00 c.c. of $N/500\text{-KI}$	Pink susp. → blue susp.	Same as above.

*Mechanism of the Colour change at the End-point.*—The colour change at the end-point can be easily explained by Fajan's views (*Z. Electrochem.*, 1923, **29**, 495). The dye, phenyl- $\alpha$ -naphthylamine-azobenzene *p*-sulphonic acid has got both acidic as well as basic character and in presence of acids, it gives violet-blue cations and in the presence of alkalis, red anions. In the  $p_H$  range of 3 to 5, both the cations as well as the anions of the dye are present in equilibrium, and hence in this range of  $p_H$ , the particles of silver halide, which are positively charged in the presence of excess of silver ions, adsorb preferentially the red anions of the dye. The anions of the dye being removed by adsorption from the supernatant suspension, the equilibrium between the acidic and basic forms of the dye is disturbed. More anions are formed to maintain the equilibrium, and more are adsorbed on the particles of the precipitate until the adsorption of the dye in the form of red anions is almost complete. Thus, the adsorption of the dye by the silver halide bodies with the development of a red colour in the presence of an excess of silver ions is so easily explained. Similarly, the particles of the silver halide precipitate have got a negative charge in the presence of excess of halide ions, and hence they preferentially adsorb the violet-blue cations of the dye and thus develop a blue shade on their surface in the presence of excess of halide ions. The mechanism of the colour change occurring in the above titrations is thus simply explained on Fajan's theory.

Thanks are due to the Scientific Research Committee of the U. P. Government for a contingency grant which partly met the cost of chemicals used in the above investigation.

## CHEMICAL EXAMINATION OF THE SEEDS OF *CITRULLUS COLOCYNTHIS*, SCHRADER. PART I. EXAMINATION OF THE OIL\*

BY R. L. ALIMCHANDANI, R. C. BADAMI AND M. C. TUMMIN KATTI

The seeds contain 21% of a pale brownish yellow oil with a bitter taste. The oil contains oleic, linoleic, myristic, palmitic and stearic acids and a phytosterol (m. p. 122-25°; acetate, m. p. 109-10°).

The seeds of Colocynth or "Bitter apple" (*Kadakavade Kayi*) are obtained from *Citrullus colocynthis*. It is a vine of the gourd family (N. O. Cucurbitaceae), native to the warmer parts of Persia, Arabia, Syria and the African and European shores of the Mediterranean. It is also cultivated in Spain and Cyprus. The plant grows wild in the North-West, the Punjab, Sind, Central and Southern India. The fruits resemble oranges in appearance with yellow and green stripes (A. F. Hill, "Economic Botany", p. 271).

Colocynth has been used medicinally for a very long time in Greek, Arabian and Indian medicine and it enters into many of the purgative pills of modern pharmacy in the form of solid extract.

The internal pulp of the dried peeled fruit is found to be useful in constipation, hepatic and abdominal, visceral and also cerebral congestions, dropsy etc; and the root in jaundice, ascites, urinary diseases, rheumatism, biliousness, constipation, fever and worms etc. The juice of the fruit mixed with sugar is a household remedy in dropsy. The oil from the seeds is used for snake-bites, scorpion-stings, any bowel complaints, epilepsy and also for the growth and blackening of hair (Nadkarni, "Indian Materia Medica"; Chopra, "Indigenous Drugs of India", pp. 121-123).

The earlier investigators (Walz, *N. Jahrb. Pharm.*, 1858, 9, 16, 225, Henke, *Arch. Pharm.*, 1883, 221, 200; Johannsen, *Z. anal. Chem.*, 1885, 24, 154; Naylor and Chappel, *Pharm. J.*, 1907, 79, 117; Grimmaldi and Prussia, *Bull. chim. Pharm.*, 1909, 48, 93; Power and Moore, *J. Chem. Soc.*, 1910, 97, 99; David, *Pharm. Ztg.*, 1928, 73, 525; Rozsa, *Ber. Ugar. Pharm.*, 1928, 4, 196; Chopra *et al.*, *Ind. J. Med. Res.*, 1929, 16, Jan.; "Indigenous Drugs of India", 1933, pp. 121-123; Agarwal and Dutt, *Curr. Sci.*, 1934, 3, 250) have all worked mostly on the pulp of the fruit excepting Grimmaldi and Prussia and Power and Moore who have done some work on the physical constants of the oil.

In view of the day to day use of the Colocynth seeds in the local veterinary medicine and the deficiency of our knowledge respecting their constituents, it seemed desirable to subject them to a more thorough chemical examination.

### EXPERIMENTAL

The seeds used for the present investigation were collected from a region near about Kurnool town in Madras Presidency.

\*This work formed part of a thesis submitted by R. C. Badami to the University of Bombay for the M.Sc. degree.

The crushed seeds (100 g.) were extracted with the following solvents successively in a soxhlet and the extracts were dried at 100°.

TABLE I

Solvent.	Extract.
Petroleum ether (b. p. 30°-60°)	25.5%
Ethyl ether	2.30
Chloroform	0.29
Ethyl acetate	0.41
Ethyl alcohol	2.62
Total 26.57%	

The petroleum ether extract gave a pale, brownish yellow oil with a bitter taste. The other extracts consist of highly colored and viscous materials about which no definite conclusions could be drawn.

#### Fatty Oil

The fatty oil was extracted with petroleum ether (b.p. 30°-60°) and the purified material had the following constants.

TABLE II

	The present authors.	Power and Moore.	Grimmaldi and Prussia
Ref. index	1 4725 (28°)	---	---
Sp. gravity	0.9257 (28°)	0.9273 (20°)	0.9289 (15°)
Acid value	3.97	---	---
Sapon value	174.0	186.7	191.7
Iodine value	117.8	126.6	120.7
Reichert-Meissl value	0.3510	---	---
Acetyl value	17.9240	---	---
Hehner value	91.64%	---	60.72%
Unsapon. matter	2.4%	---	---

#### Mixed Fatty Acids

The oil (500 g.) was saponified and the resulting hard soap was powdered and extracted with ether in a soxhlet apparatus to obtain the unsaponifiable matter. The residual soap powder was freed from ether and the fatty acids were liberated and purified. The mixed free fatty acids were found to have the following constants: mixed fatty acids, 91.0, mean mol. wt. of the mixed acids, 279.45; iodine value, (Hanus), 121.0.

About 300 g. of the mixed fatty acids were separated into their saturated and unsaturated components by Twitchell's lead-salt-alcohol method (*Ind. Eng. Chem.*, 1921,

18, 806). During the course of separation, a brown, resinous, semi-solid material, which was insoluble even in boiling alcohol, remained stuck to the bottom of the flask. The liberated saturated and unsaturated acids had the following constants.

TABLE III

	Saturated acids.	Unsaturated acids.
Per cent.	12.12	87.88
Mean mol. wt.	267.3	289.4
Iodine value (Hanus)	4.879	132.0

#### *Liquid Fatty Acids*

A portion of the liquid acids was brominated according to the method of Eibner and Muggenthaler (Lewkowitsch, "Chemical Technology and Analysis of Oils and Fats", 6th Ed., Vol. I, p. 585). A white crystalline solid, tetrabromostearic acid (m.p. 113-114°; M.W. 597.5) was obtained, indicating the presence of linoleic acid in the liquid acid mixture. From the filtrate no hexabromostearic acid could be isolated.

Another portion of the liquid acid mixture was oxidised by cold 1% alkaline potassium permanganate solution according to the method of Lapworth and Mottram (*J. Chem. Soc.*, 1925, 1628). From the mixture of hydroxy-acids, thus obtained, the following were isolated.

TABLE IV

Acid.	M.p.	M.W. (found).	M.W. (calc.)
Dihydroxystearic acid	135°	315.0	316.4 (oleic)
Tetrahydroxystearic acid	167-68°	347.2	348.4 (linoleic)

Thus, the presence of oleic and linoleic acids among the unsaturated acid mixture was established.

#### *Solid Fatty Acids*

The mixture of solid acids was esterified with methyl alcohol in the usual manner and 40 g. of the saturated methyl esters were fractionally distilled at a pressure of 5 mm.

Fraction No.	Temp. range.	Wt	M.W. of acids.	Fraction No.	Temp. range.	Wt.	M W. of acids.
I	below 165°	3.4 g.	225.4	VI	182°-185°	8.6 g.	282.2
II	165°-170°	1.0	251.4	VII	185°-187°	2.7	284.5
III	170°-175°	4.6	256.7	VIII	187°-188°	2.5	285.2
IV	175°-180°	4.2	259.2	IX	above 188° (residue)	7.9	292.3
V	180°-182°	5.1	271.2	Total		40.0	

*Fraction I.*—The crude acid from this fraction after repeated crystallisations from 80% alcohol gave an acid melting at 50-51°, with a molecular weight of 226.7, identified as myristic acid. A mixed melting point determination with a laboratory sample of myristic acid did not change the melting point.

*Fraction II-IV.*—The acids liberated from these fractions after repeated crystallisations from 80% alcohol yielded pure palmitic acid (m.p. 60-61°, M. W. 256.4). Mixed with pure palmitic acid, the melting point remained unchanged.

*Fraction V.*—This gave an acid which corresponded to an eutectic mixture of palmitic and stearic acids. Repeated crystallisations from various solvents gave a product melting at 56-57° (M.W. 267).

*Fraction VI-IX.*—The acids liberated from these fractions after repeated crystallisations from 92% alcohol gave pure stearic acid (m p. 69-70°, M.W. 283.6). The melting point remained unchanged on mixing this acid with pure stearic acid.

Thus the saturated acids were found to consist of myristic, palmitic and stearic acids.

#### *Unaponifiable Matter*

This was mostly an oily mass with a small quantity of fine crystals interspersed in it. From the ether extract of the unaponifiable matter, a phytosterol (m p. 122-25°) was obtained in a colorless and pure state after repeated treatment with animal charcoal and recrystallisations from 75% alcohol. This compound gave all the characteristic colour tests of phytosterols. Its acetate melted at 109-110°.

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## CHEMICAL EXAMINATION OF THE SEEDS OF *CITRULLUS COLOCYNTHIS*, SCHRADER. PART II\*

By R. L. ALIMCHANDANI, R. C. BADAMI AND M. C. TUMMIN KATTI

The seeds are intensely bitter and contain an alkaloid, a polysachharide or a glucoside, an enzyme or enzymes reducing  $\beta$ -glucosides and tannin. The seeds contain 21% of a pale brownish yellow oil, phytosterolin (Ipuranol), two phytosterols, two hydrocarbons and also saponin material and a sugar. From the active bitter principle a very small amount of an yellow crvstalline compound melting at 176° has been isolated.

Power and Moore (*J. Chem. Soc.*, 1910, 97, 99) examined the pulp of the fruit (Turkish variety) separately from the seeds and the following substances were isolated: citrullol, a dihydric alcohol; an amorphous alkaloidal substance possessing an extremely bitter taste and representing one of the purgative principles of the fruit.  $\alpha$ -elaterin, a small amount of hentriacontane, a phytosterol and a mixture of fatty acids. They found the seeds comprising 75.5% of the peeled fruit to contain traces of an alkaloidal principle, a small amount of an enzyme hydrolysing  $\beta$ -glucosides, and fatty oil.

The present investigation deals with the examination of the seeds only and the following compounds have been isolated: a phytosterolin (Ipuranol), two phytosterols, one melting at 122-24° and the other at 98-100°; two hydrocarbons, one melting at 59-60° and the other at 54-56°; also saponin material and a sugar. The seeds are found to be intensely bitter and contain an alkaloid, polysachharide or a glucoside, an enzyme or enzymes reducing  $\beta$ -glucosides, and tannin. From the active bitter principle a very small amount of an yellow crystalline compound (m. p. 176°) has been isolated. The fatty oil has been completely investigated separately (cf. Part I, this issue, p. 515).

It will be observed from the literature (cf. Part I) that there has been no thorough chemical examination of the *Colocynthis* seeds. Most of the earlier investigators confined their work to the investigations of the pulp of the fruit. In view of the medicinal value of *Colocynthis* in modern pharmacy and the absence of any work on the Indian *Colocynthis*, the present investigation was undertaken.

### EXPERIMENTAL

#### *Preliminary Examination*

**Test for Alkaloids.**—The crushed seeds (15 g.) were digested with Prollius' solution for about 2 hours and the mixture filtered. The filtrate gave tests for the presence of alkaloids.

The crushed seeds (15 g.) were shaken for 5 minutes with 150 c.c. of a mixture of chloroform and ethyl ether. Concentrated ammonia (5 c.c.) and water were then added and the mixture shaken for about 2 hours and 15 c.c. of water were added and filtered. The filtrate was extracted with 1% sulphuric acid solution. The acid extract was made ammoniacal and extracted with the same solvent mixture as above and finally extracted with 1% sulphuric acid solution. This acid extract showed the presence of alkaloids when tested with the usual alkaloid reagents.

\*This work formed part of a thesis submitted by R. C. Badami to the University of Bombay for the M.Sc. degree.

*Test for Enzymes.*—The crushed seeds (100 g.) after extraction with petroleum ether were dried and shaken with water for about 12 hours. The supernatant liquid was then expressed and filtered with difficulty. A quantity of redistilled rectified spirit was added to the filtrate, when a thick, light colored precipitate was produced which was filtered and washed with a little alcohol and dried in a desiccator.

This substance was found to contain an appreciable amount of reducing substances and some inorganic material. It reduced  $\beta$ -glucoside indicating the presence of an enzyme.

*Steam distillation.*—The crushed seeds (200 g.) were distilled with steam and about 700 c.c. of the distillate were collected. The distillate, which was not acidic, was then extracted with ether. The extract was dried and the solvent removed. A very small amount of a pale yellow oily mass was thus obtained which could not be identified.

*Test for Starch, other Carbohydrates, Tannins, etc.*—The crushed seeds (15 g.) were digested with water on a hot water-bath for about half an hour and the supernatant liquid was decanted and filtered. The filtrate gave tests for the presence of tannins and a reducing material. A portion of the filtrate, on hydrolysis, showed the presence of a good amount of a polysachharide or a glucoside. This latter reduction may be due to the glucose formed by the hydrolysis of the glucoside supposed to be present in the seeds. The bitter taste of the original filtrate indicates that a glucoside is at least partially responsible for the heavy reduction after hydrolysis.

The crushed seeds (4 kg.) were extracted with redistilled rectified spirit in a modified soxhlet apparatus (cf. Tummin Katti, this *Journal*, 1930, 7, 210). The extract was completely freed from the solvent when a dark brown, viscous material, bitter in taste, was left over. This material was spread on fine filter-paper pulp, dried and extracted in a soxhlet (*loc. cit.*) successively with petroleum ether (b.p. 30°-60°), ethyl ether, chloroform, ethyl acetate and ethyl alcohol, and the various extracts were examined completely.

#### *Petroleum Ether Extract*

This is a brown viscous material and has a faint bitter taste. In order to isolate this bitter principle, the extract was shaken with 90% alcohol and the alcohol was removed and filtered.

(A) *Alcohol-soluble portion.*—The solvent was removed and the residue, dissolved in chloroform, was poured into a large volume of petroleum ether (b.p. 60°-80°). There was no precipitate, not even a turbidity on keeping the mixture overnight. Evidently the bitter principle did not come down in the petroleum ether extract.

The mixture of solvents was then distilled off and the residue saponified. The soap was dried on fine, dry, filter-paper pulp and extracted with ether in a soxhlet. Thus the above material was separated into (i) sodium salts of the fatty acids from the saponifiable material and (ii) ether-soluble unsaponifiable matter. The former material was not examined further since the fatty oil has been completely investigated. The latter material was washed free of soap and the solvent removed. A white solid material separated on concentrating the extract, which was removed by filtration; the filtrate on standing deposited some more of the solid material.

*Isolation of Phytosterolin (Ipuranol, m.p. 287°-90°).*—The white solid material recovered from above was refluxed with charcoal and crystallised from 95% alcohol.



The white shining crystals gave all the colour reactions of phytosterols, m.p. 287-90°. The acetate melted at 162-64°. This compound is Ipuranol in conformity with the substance isolated by Tummin Katti (*loc. cit.*) from the seeds of *Caesalpinia bonducella* and by Power and co-workers from a number of plant materials.

*Isolation of a Phytosterol* (m. p. 122-24°).—The filtrate from above after removal of the solid material (Ipuranol) was freed from the solvent and the pale yellow viscous residue was digested with charcoal and crystallised from 75% alcohol, as white glistening solid, m.p. 122-124°, which gave all the colour tests of phytosterols. It gave an acetate, m.p. 109-10°.

(B) *Alcohol-insoluble portion*—The dark viscous oil was saponified and the resulting soap was spread on filter-paper pulp, dried and extracted with ether. During the course of extraction, a white solid powder separated out.

*Unsaponifiable Matter. Isolation of a Phytosterol* (m.p. 98-100°).—The ether-insoluble white powder from above was refluxed with charcoal and crystallised from 95% alcohol. The snow-white crystals melted at 98-100° and gave all the colour tests of phytosterols.

*Isolation of a Hydrocarbon* (m.p. 59-60°).—The clear, light yellow, ether-soluble portion from above was washed free of soap and the solvent distilled. The viscous residue was crystallised from 80% alcohol when beautiful snow-white glistening plates melting at 59-60° were obtained. The insolubility of this solid material in concentrated sulphuric acid even after warming on the water-bath suggested that it might be a saturated hydrocarbon, but the quantity was too small for further analysis.

#### *Ethyl Ether Extract*

The syrupy, viscous, dark red extract, freed from the last traces of ether, was found to be intensely bitter. The extract was dissolved in chloroform and poured into a large excess of petroleum ether (b.p. 60°-80°). A pale yellow powder immediately separated out. This powder was carefully filtered and washed with petroleum ether. After some time, the powder set to a dark brown, resinous mass. This material is intensely bitter.

The bitter principle softens at 103° and completely melts at 112°. It is readily soluble in chloroform, alcohol, glacial acetic acid and benzene; slightly soluble in water and sparingly soluble in petroleum ether.

Elementary analysis of the bitter principle proved the presence of nitrogen and absence of sulphur and halogens.

The bitter principle gave tests for the presence of an alkaloid and a reducing material. A portion of the bitter principle, on hydrolysis, gave tests for the presence of a considerable amount of a polysaccharide. This may be due to the glucose formed by the hydrolysis of the glucoside supposed to be present in the bitter principle.

These tests indicate the presence of an alkaloid, a reducing material and a polysaccharide or a glucoside in the bitter principle.

*Isolation of an yellow crystalline compound*.—A portion of the bitter material was dissolved in alcohol and treated with an alcoholic solution of lead acetate. The precipitate was filtered and the filtrate freed from excess of lead by passing a current of hydrogen sulphide. The filtrate from this was evaporated to a syrup and refluxed

with acetic ether for several hours. On cooling, a small amount of an yellow crystalline material separated out. This was filtered and the filtrate on concentration yielded a little more of this solid. This compound melted at  $176^{\circ}$ . Further examination of this crystalline material could not be undertaken for want of sufficient material.

The mixture of solvents (chloroform and petroleum ether) after removing all the bitter principle was distilled, when a very small amount of a pale yellow viscous oil was obtained.

#### *Chloroform Extract*

The dark brown, syrupy extract was found to be slightly bitter. Attempts to separate any bitter principle from this extract were, however, unsuccessful. On crystallisations from 80% alcohol a fraction of a white solid was obtained, m.p.  $54-56^{\circ}$ . Its insolubility in concentrated sulphuric acid even after warming on a water-bath, suggested that it might be a saturated hydrocarbon, but the quantity was too small to permit further investigation. No other compound could be separated from this extract.

#### *Ethyl Acetate Extract*

The brown extract was found to be slightly bitter. This was refluxed with charcoal and crystallised from 95% alcohol when a white powdery substance separated out. This material was too small for further work. No other compound could be isolated from this extract.

#### *Alcohol Extract*

The dark brown extract after complete removal of the solvent was dissolved in water. It was bitter in taste. The aqueous solution was treated with basic lead acetate and the pale yellow precipitate was filtered and washed with water.

*Identification of Saponin.*—The precipitate from above was suspended in water and decomposed by passing a current of hydrogen sulphide and filtered. The filtrate on concentration under reduced pressure gave a very small amount of a dark red semi-solid and an yellow liquid which frothed considerably on shaking. The semi-solid material was found to be bitter. No definite crystalline compound could be isolated from this semi-solid material. The yellow solution on hydrolysis reduced Fehling's solution after heating for a long time and keeping for several hours. These properties indicate the presence of a saponin material in the liquid.

*Identification of Sugar.*—The filtrate and the washings from above, after removing the precipitates of lead salts, were mixed together, delead, filtered, and the filtrate concentrated to a small bulk, when a very small amount of white shining needles separated, which were removed by filtration. The filtrate was then digested with alcohol (redistilled rectified spirit) for over 2 hours and cooled. No compound separated from this. A portion of this filtrate on hydrolysis gave a faint indication of the presence of a reducing material.

The needle-shaped crystals from above had a very faint sweet taste and their melting point was above  $300^{\circ}$ .

The syrupy liquid after removal of the needle-shaped crystals, gave an osazone, m.p.  $204-205^{\circ}$ . No other compound could be isolated from the alcohol extract.

## CHEMICAL EXAMINATION OF THE SEEDS OF *JATROPHA GLANDULIFERA*, ROXB.\*

By R.L. ALIMCHANDANI, R.C. BADAMI AND M.C. TUMMIN KATTI

The seeds contain 50% of kernels and 22% of a pale, brownish yellow oil. They are found to contain palmitic, stearic, oleic and linoleic acids; sitosterol (m.p. 131-35°), a phytosterol (m.p. 122-24°), tannin, glucose (osazone, m.p. 203-204°) and a large amount of a reducing material together with some resinous substance. No acid corresponding to or similar in structure as ricinoleic acid could be isolated from the unsaturated acids.

*Jatropha glandulifera* is a shrub common at the outskirts of villages in Bengal, Burma, the Northern Circars and Deccan. It is found to grow abundantly on the bunds of tanks. The plant is also prevalent in the waste lands of tropical Africa.

The constituents found in the plant are similar to those of *Jatropha curcas* and also in action. It is purgative, counter-irritant and stimulant. The leaves have a bad taste, act as emmenagogue and are analgesic. They lessen inflammation, asthma, bronchitis, lumbago, and are useful in scorpion-stings. The root is good for piles. The root, brayed with water, is given to children suffering from abdominal enlargements. It purges and is said to reduce glandular swellings. The juice of the plant is used to remove films from the eyes. The fixed oil from the seeds has purgative properties. It is applied to joints in chronic rheumatism, chronic ulcerations, sinuses, ringworm, paralysis and also to foul wounds (Kirtikar and Basu, "Indian Medicinal Plants", 2nd Ed., Vol. III, pp. 2241-2242; Nadkarni, "Indian Materia Medica"; Menon, *J. Soc. Chem. Ind.*, 1910, 29, 1428).

The only mention in the literature regarding the chemical examination of *Jatropha glandulifera* is that of Menon (*loc. cit.*). He has determined some physical constants of the fixed oil from the seeds prepared 4 or 5 years previously and his work is of a very preliminary nature.

The plant belonging to Euphorbiaceae and the oil being a drastic purgative, the latter is usually surmised to be similar to castor oil, particularly with reference to the presence of ricinoleic or other acid of a similar structure. This view is shown to be incorrect in the case of *Jatropha curcas* by Tummin Katti, Alimchandani and Gouder (*J. Univ. Bombay*, 1945, 14, Part III, p. 34). The present investigation was taken up to throw further light on the purgative principle of the seeds with special reference to the nature of the fatty acids in general and of the unsaturated acids in particular.

### EXPERIMENTAL

The seeds for the present investigation were collected from places round about Kurnool in Madras Province.

The seeds contain 50% of kernels and 22% of a pale, brownish yellow oil.

\* This work formed part of a thesis submitted by R.C. Badami to the University of Bombay for the M.Sc. degree.

*Preliminary Examination*

The crushed seeds (100 g.) were extracted successively with the following solvents and the extracts dried at 100°.

				Extract.
Petroleum ether (b.p. 30°-60°)	...	...	...	22.2%
Ethyl ether	..	...	..	2.2
Chloroform	..	...	..	0.4
Ethyl acetate	...	...	...	0.6
Ethyl alcohol	...	...	...	2.5
Total				27.9

The seeds were not found to contain any alkaloidal material when tested with Prollius fluid. On distilling 200 g. of the crushed seeds with steam, a very small amount of a pale yellow, oily material was obtained. The aqueous extract of the seeds contained tannins, some reducing material and polysachharides.

The powdered seeds (2.5 kg.) were percolated with cold rectified spirit and the solvent removed from the percolate by distillation under reduced pressure. The syrupy, dark brown residue was dried on fine shreads of filter-paper pulp and extracted successively with petroleum ether, ethyl ether, chloroform, ethyl acetate and ethyl alcohol, and the extracts were examined separately.

*Petroleum Ether Extract.*—The solvent-free extract was digested with 90% alcohol. (a). The alcohol-soluble portion was saponified and the dry soap extracted with ether. The ether-soluble portion was washed free of soap and digested with charcoal for an hour. The pale yellow extract on repeated crystallisations from 75% alcohol yielded white, shining crystals (m.p. 122-24°) which gave all the characteristic colour tests of phytosterols; the acetate, m.p. 109-10°. The ether-insoluble sodium salts of the fatty acids, mixed with the corresponding salts of the fatty acids from the oil obtained by direct petroleum ether extract of a fresh portion of powdered seeds, were examined separately.

(b). The alcohol-insoluble portion, when worked in like manner as above, gave a phytosterol (m.p. 122-24°; acetate, m. p. 109-10°) and no other compound could be isolated.

*Ethyl Ether Extract.*—The solvent-free extract was dissolved in chloroform and poured into a flask containing a large excess of petroleum ether (b. p. 60°-80°). No solid separated, but only a brown, viscous, resinous material settled to the bottom of the flask.

This petroleum ether-insoluble resinous material had the consistency of rubber. It had no taste and it did not reduce Fehling's solution. All attempts to get a definite crystalline material from this substance were unsuccessful.

The petroleum ether-soluble portion gave a small amount of a dark oily mass from which nothing definite could be isolated.

*Chloroform Extract.*—The solvent-free, pale brown extract was dried on a water-bath and dissolved in 80% alcohol and digested with charcoal. On concentrating the filtrate

and keeping overnight, a few white crystalline particles were found to float on the surface; but on further concentration, these particles turned yellow and set to a resinous mass. A portion of this extract reduced Fehling's solution with difficulty but on hydrolysis the reduction was instantaneous, indicating the presence of a polysaccharide. However, all attempts to isolate a definite crystalline compound were unsuccessful.

*Ethyl Acetate Extract.*—After complete removal of the solvent, the dark brown extract, which was slightly sweet to taste, was digested as above with charcoal, and the filtrate on concentration did not deposit any crystalline material. It readily reduced Fehling's solution, showing the presence of a considerable amount of some reducing material. Nothing crystalline could be isolated from this extract.

*Alcohol Extract.*—After removal of the last traces of the solvent by distillation under reduced pressure, the sweet, syrupy, dark brown residue was dissolved in water and the solution treated with basic lead acetate. The pale yellow precipitate was filtered and washed with water. It was suspended in water and delead. No solid separated on concentrating the filtrate. It reduced Fehling's solution. A portion of the filtrate on treating with ferric chloride solution was coloured bluish green indicating the presence of tannin. The presence of tannin was further confirmed on treating another portion of the filtrate with potassium dichromate solution yielding a brown precipitate.

*Identification of Sugar.*—The filtrate and washings, after removing the precipitates of lead salts, were mixed together and delead. The filtrate was concentrated to a syrup. This syrupy residue was distinctly sweet to taste. On digesting the syrup for about 2 hours with redistilled rectified spirit, a very small amount of a white crystalline solid separated which was sweet to taste. This solid could not be worked further for want of sufficient material. However, a small amount of the solution of these crystals readily reduced Fehling's solution.

The syrupy residue, left after removal of the rectified spirit from the filtrate from above, yielded an osazone which on recrystallisation from pyridine and alcohol, melted sharply at 203-204°, indicating the presence of glucose. No other compound could be isolated from the alcoholic extract.

### Fatty Oil

The crushed seeds (2 kg.) were extracted with petroleum ether (b.p. 30°-60°) in a modified soxhlet (Tummin Katti, *J. Indian Chem. Soc.*, 1930, 7, 210) continuously for about 24 hours and the solvent removed. The purified oil had the following constants :

Ref. index at 27°	...	.. 1.4672	Iodine value (Hanus)	...	... 121.5
Sp. gr. at 27°	...	... 0.9216	Reichert-Meissl value	...	... 0.5234
Sapon. value	...	.. 209.1	Hehner value	..	... 91.6 %
Acetyl value	...	... 16.46	Unsapon. matter	...	... 1.53 %

*Mixed Fatty Acids*

The oil (205 g.) was saponified and the resulting dry hard soap was extracted with ether in a soxhlet to obtain the unsaponifiable matter. The residual soap powder was freed from ether and mixed with the sodium salts of fatty acids obtained from the alcoholic extract of the seeds, as mentioned before, and the fatty acids were liberated and purified. The mixed free fatty acids had the following constants: mixed fatty acids, 91.7 %; mean M.W., 275.5; iodine value (Hanus), 126.2.

The mixed free fatty acids (150 g. approx.) were separated into saturated and unsaturated acids by Twitchell's lead-salt-alcohol method (*Ind. Eng. Chem.*, 1921, **13**, 806). The liberated saturated and unsaturated acids had the following constants:

	Saturated.	Unsaturated.
Percentage	13.1	86.9
Mean M.W.	266.9	287.0
Iodine value (Hanus)	5.2	135.0

*Liquid Fatty Acids*

The liquid acids were esterified with absolute methyl alcohol in the usual manner and 49 g. of these methyl esters were distilled under 10 mm. pressure.

Fraction.	Temp. range.	Wt.	M.W.	Iodine value (Hanus).
I	up to 150°	2.3 g.	240.0	60.4
II	150°-165°	1.5	255.5	68.9
III	165°-185°	2.4	280.0	89.7
IV	185°-195°	5.6	286.2	100.2
V	195°-209°	18.2	287.4	102.4
VI	209°-210°	4.8	288.1	114.3
VII	Residue	14.2	288.6	119.8

Total 49.0

Fractions I and II probably consisted of decomposition products; and hence, fractions III—VII were selected for further investigation.

Fractions III—VI were mixed together and about 5 g. of the ester mixture were saponified and oxidised according to the method of Lapworth and Mottram (*J. Chem. Soc.*, 1925, 1628). From the mixture of hydroxy-acids, thus obtained, the following were isolated.

Acids.	M.p.	M.W. (found).	M.W. (calc
Dihydroxystearic	134°-135°	315	316.4 (oleic)
Tetrahydroxystearic	154°-155°	347	348.4 (linoleic)

A portion of fraction VII was saponified and the liberated acids were brominated according to the method of Lïbner and Mugganthaler (Lewkowitsch, "Chemical Technology and Analysis of Oils and Fats", 6th Ed., Vol. I, p. 585). A white crystalline compound, tetrabromostearic acid (m. p. 113-14°) was obtained, indicating the presence of linoleic acid in the liquid acid mixture. From the filtrate no hexabromostearic acid could be isolated.

Thus the liquid unsaturated acids were found to contain only oleic and linoleic acids.

#### *Solid Fatty Acids*

The mixture of solid acids were converted into their methyl esters in the usual manner and 19 g. of the ester mixture were distilled under 15 mm. pressure.

Fraction.	Temp. range	Wt.	M.W.	Fraction.	Temp. range.	Wt.	M.W.
I	below 194°	3.23 g.	259.3	V	197°-199°	2.90 g.	285.4
II	below 194°	2.83	256.2	VI	199°-202°	1.80	286.9
III	194°-195°	2.12	268.2	VII	202° and above	1.39	286.3
IV	195°-197°	3.45	283.5	VIII	Residue.	1.28	286.7
Total 19.00							

*Fractions I & II.*—From each of these fractions pure palmitic acid (m.p. 61.5°; M.W. 255.4) was isolated as the principal constituent. The identity of the palmitic acid was further established by taking a mixed m.p. with an authentic pure sample.

*Fraction III.*—From this fraction a small amount of palmitic acid (m.p. 61°; M.W. 257) was isolated. The filtrate gave an acid, m.p. 58-59°, with M.W. of 267, probably a mixture of palmitic and stearic acids.

*Fraction IV.*—From this fraction an acid which melted at 63-69° and with a M.W. of 282 was isolated. The filtrate gave an acid (m.p. 57-58°; M.W. 270), which could not be improved further.

*Fractions V - VII.*—From each of these fractions pure stearic acid (m.p. 68-69°; M.W. 284.3) was isolated. The melting point remained unchanged on mixing with pure stearic acid.

Thus from the solid acid mixture, only palmitic and stearic acids could be isolated.

*Unsaponifiable Matter*

This was a reddish, oily, semi-solid material. On digesting repeatedly with charcoal in 95% alcohol and crystallising the product, pure white crystalline compound answering to all the colour tests of phytosterols was obtained. It melted at  $134-35^{\circ}$  and yielded an acetate melting at  $121-22^{\circ}$ . This substance is therefore identified as sitosterol. No other compound could be isolated from the mother-liquor.

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## CONDITION OF SPARINGLY SOLUBLE SALTS OF COPPER AND SILVER IN GELATIN

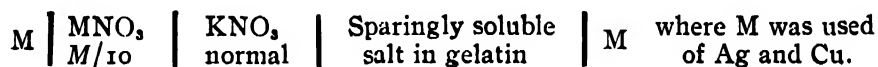
By A. C. CHATTERJI AND M. C. RASTOGI

The condition of various sparingly soluble salts of silver and copper in gelatin sol has been studied. The E. M. F. of these salts in gelatin at various concentrations was measured and the percentage of cations of the respective salts calculated. The low percentage definitely indicates that the sparingly soluble substance is not in the ionic condition as is required for supersaturation, but is in the colloidal state.

Among the several theories of Liesegang ring formation "Supersaturation theory" of Wilhelm Ostwald ("Lehrbuch der allgemeinen Chemie", Leipzig, 2nd Ed., ii, p. 778) and "Coagulation theory" of Dhar and Chatterji (*Kolloid Z.*, 1922, **31**, 15; 1925, **57**, 2) are of general application. The essential difference between these two is that the sparingly soluble substance, immediately before the precipitation, exists in highly supersaturated state according to Ostwald, while according to the latter authors it remains as a sol. Although Hedges and Bradford (cf. *Chem. Ind.*, 1929, **48**, 233) have suggested that there may be very little difference between the above two conditions, yet it is of vital importance to know the exact conditions of the salt prior to the formation of the rings. Williams and Mackenzie (*J. Chem. Soc.*, 1920, **117**, 844), Bolam and Mackenzie (*Trans. Faraday Soc.*, 1926, **22**, 151), Bolam and co-workers (*ibid.*, 1928, **24**, 463; 1930, **26**, 133, 1933, **29**, 84), Desai and co-workers (*ibid.*, 1932, **28**, 449; *J. Indian Chem. Soc.*, 1934, **11**, 45) and Andrew van Hook (*J. Phys. Chem.*, 1938, **42**, 1191; 1940, **44**, 422; 1941, **45**, 1194) are of the opinion that the salt is in the ionic condition, whereas Sen and Dhar (*Kolloid Z.*, 1924, **34**, 270), Dhar and Chatterji (*loc. cit.*; *Trans. Faraday Soc.*, 1927, **23**, 23), Chatterji and Dhar (*J. Indian Chem. Soc.*, 1928, **5**, 175) and Chatterji and J. M. Dhar (*ibid.*, 1930, **7**, 177) do not agree with the above view, and regard the sparingly soluble salt to be mainly in the colloidal state. The present work has been undertaken in order to have a quantitative idea of the condition of the sparingly soluble salts in presence of gelatin. Silver chromate in gelatin or lead iodide in agar agar has already been investigated in greater detail. It has been suggested that these salts are in the ionic state. These salts form either complexes or are soluble in the excess of either of the reagents and it presents difficulties in interpreting the results. It has been found that the sparingly soluble salts of this type give a large percentage of ions and dissolve in excess of one of the reagents. To test further this point a large number of the sparingly soluble salts have been examined by E. M. F. method.

## E X P E R I M E N T A L

The work has been done on the same lines as of Chatterji and J. M. Dhar (*loc. cit.*). The same preparation of gelatin was used throughout the experiments. The results obtained are given below. The cell used was as following :



Concentration of gelatin used was 5% in each experiment.

TABLE I

With silver ferrocyanide.

No.	E. M. F.	Conc. of the salt.	Conc. of Ag present as ions.	% Ag as ions.
1	0.2268 volt	10,000 $N \times 10^{-6}$	11.72 $N \times 10^{-6}$	0.1172
2	0.2497	5,000	4.72	0.0944
3	0.2728	2,500	1.91	0.0764
4	0.2862	1,250	1.14	0.0890

With silver ferricyanide.

1	0.3251	100,000 $N \times 10^{-7}$	2.371 $N \times 10^{-7}$	0.0023
2	0.3153	50,000	3.476	0.0069
3	0.3149	25,000	3.573	0.0143
4	0.3052	12,500	5.225	0.0418

With silver thiosulphate.

1	0.2324 volt	10,000 $N \times 10^{-6}$	9.399 $N \times 10^{-6}$	0.0939
2	0.2570	5,000	3.532	0.0706
3	0.2446	2,500	5.754	0.2310
4	0.2595	1,250	3.192	0.2546

With silver iodate.

1	0.1608	100 $N \times 10^{-4}$	1.483 $N \times 10^{-4}$	1.483
2	0.1487	50	2.583	5.166
3	0.1499	25	4.335	17.340
4	0.1518	12.5	2.302	18.416

TABLE II

With copper ferrocyanide.

No.	E. M. F.	Conc. of the salt	Conc. of Cu present as ions.	% Cu ions.
1	0.06751 volt	1,000 $N \times 10^{-6}$	17.06 $N \times 10^{-6}$	1.706
2	0.08223	500	5.29	1.058
3	0.09098	250	2.61	1.055
4	0.10280	125	1.02	0.820

With copper ferricyanide.

1	0.08923	10,000 $N \times 10^{-6}$	3.01 $N \times 10^{-6}$	0.301
2	0.11300	5,000	4.07	0.081
3	0.12040	2,500	2.01	0.080
4	0.12600	1,250	1.62	0.130

With copper borate.

1	0.08901	1,000 $N \times 10^{-6}$	1.538 $N \times 10^{-6}$	0.153
2	0.08620	500	1.979	0.396
3	0.09066	250	0.654	0.262
4	0.10200	125	0.541	0.432

With copper hydroxide.

1	0.05546	1,000 $N \times 10^{-6}$	1.106 $N \times 10^{-6}$	0.110
2	0.06146	500	1.311	0.262
3	0.07451	250	0.976	0.390
4	0.08720	125	0.901	0.721

With copper arsenate.

1	0.09814	1,000 $N \times 10^{-6}$	15.87 $N \times 10^{-6}$	1.587
2	0.09094	500	13.57	2.714
3	0.09462	250	4.81	1.926
4	0.09594	125	1.77	1.418

## DISCUSSION

From the foregoing results it will be found that in the cases of silver ferrocyanide, ferricyanide, thiosulphate, and copper ferrocyanide, ferricyanide, borate, hydroxide, and arsenate the percentage of the respective cation, which is in ionic condition, is small, whereas in the case of silver iodate, it is found that the percentage of silver in ionic condition is more than that found in the other group. It is about 18% in the smallest concentration used. It is 10 times the solubility. The mere fact that many sparingly

soluble salts, which give quite good rings, are not found in the ionic state, whereas only a few salts like silver chromate, lead iodide and silver iodate show signs of existing in appreciable quantity in the ionic state, causes considerable doubt on the general hypothesis that every sparingly soluble salt must be in supersaturated condition. Further work in this direction is in progress in this laboratory with a view to extending the investigation to a large number of sparingly soluble salts in order to elucidate the true cause of the phenomenon of some salts indicating a larger percentage to be in the ionic state than is the case with most other salts.

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## APPLICATION OF MIXTURE LAW TO RHEOCHOR. PART III.

BY M. V. SABNIS, W. V. BHAGWAT AND H. G. SILAWAT

The application of mixture law to rheochor for non-associated liquid in associated solvent has been investigated. The non-associated liquids investigated are benzene, toluene, chloroform and carbon tetrachloride in the associated solvent, methyl alcohol. It is observed that the law is applicable in all cases. For chloroform, however, for low concentrations the deviation is somewhat more.

In previous papers (this *Journal*, 1944, 21, 29; 1946, 23, 349; 1948, 25, 165, 575) the application of mixture law to rheochor, when liquid mixtures are considered, has been discussed. According to Hammick and Andrew (*J. Chem. Soc.*, 1929, 754) the liquid mixtures have been divided into three groups: (i) non-associated solutes in non-associated solvents, (ii) associated liquids in non-associated solvents and (iii) associated liquids in associated solvents. The group (iii) was investigated by us in Parts I and II (*loc. cit.*). In this paper we have extended this work to non-associated liquids in associated solvents (group ii).

To obtain a correct idea of the applicability of the mixture law, it is necessary to study the mixtures over the whole range of molar concentrations *i. e.* from 0 to 1. Similar procedure was followed by Hammick and Andrew (*loc. cit.*) in the case of parachor of liquid mixtures. In case of rheochor, however, it is necessary to investigate the applicability at different temperatures, since the rheochor values change with temperature and rheochor constants are determined from the values as obtained at boiling point. Following tables show our results.

*Non-associated Liquids in Associated solvents*

$\alpha$ ,  $D$ ,  $\eta$ ,  $M_m$ ,  $R_m$  and  $R_x$  have the same significance as given in previous papers.

TABLE I  
*Benzene in methyl alcohol.*

Temp. = 30°.

$\alpha$ .	$D$ .	$\eta \times 10^3$ .	$M_m$ .	$R_m$ .	$R_x$ .
0.0000	0.7903	5.60	32.00	50.30	—
0.0572	0.7990	5.62	34.63	53.80	112.0
0.1598	0.8127	5.64	39.38	60.18	111.8
0.2552	0.8221	5.60	43.73	65.98	111.7
0.3449	0.8307	5.63	47.87	72.61	111.5
0.4474	0.8420	5.59	53.36	78.47	111.2
0.7425	0.8551	5.46	66.16	95.68	111.4
0.8277	0.8606	5.40	70.08	100.78	111.3
1.0000	0.8646	5.70	78.00	—	112.0

TABLE I (contd.)

Temp. = 40°.

$x$ .	$D$ .	$\eta \times 10^3$ .	$M_m$ .	$R_m$ .	$R_x$ .
0.0000	0.7823	4.90	32.00	50.01	—
0.0572	0.7903	5.00	34.63	53.59	111.1
0.1598	0.8037	4.91	39.38	59.77	110.3
0.2552	0.8139	5.05	43.73	65.67	110.2
0.3449	0.8219	5.07	47.87	71.08	110.7
0.4474	0.8321	4.78	53.36	77.98	109.9
0.7425	0.8468	4.69	66.16	94.82	110.4
0.8277	0.8534	4.90	70.08	100.20	110.6
1.0000	0.8537	4.90.	78.00	—	111.4

Temp. = 50°.

0.0000	0.7747	4.16	32.00	49.74	—
0.0572	0.7817	4.15	34.63	52.91	109.6
0.1598	0.7971	4.11	39.38	58.80	109.0
0.2552	0.8070	4.18	43.73	64.54	109.2
0.3449	0.8131	4.05	48.00	70.28	109.3
0.4474	0.8238	4.14	53.36	77.37	109.6
0.7425	0.8385	4.11	66.16	94.04	109.6
0.8277	0.8420	4.13	70.08	99.38	109.8
1.0000	0.8447	4.15	78.00	—	109.2

The mixture law seems to be completely applicable in case of benzene, dissolved in methyl alcohol, the values of  $R_x$  as obtained is practically constant although the molar fraction of benzene is changed from 0 to 1 for the same temperature. The value of  $R_x$  falls with increase of temperature from 112 to 110. The drop in the value of  $R_x$  is gradual and is consistent with the fall in values of  $R$  of pure liquid with temperature. The following table with pure liquid will illustrate this.

TABLE II

Temp. ...	60°	80°	100°	140°	180°	240°
$R$ (benzene, b.p. 88°)	110.4	110.4	109.8	109.8	109.2	—

It will be observed that for benzene, temperature has very little effect on  $R$ . This is also borne out in the mixtures we have studied at different temperatures. Our value of  $R_x$  is comparable with the value of  $R$  given in the above table (Friend and Hargreave, *Phil. Mag.*, 1921, iv, 34, 943, 644). The value of  $R_x$  cannot be compared with the calcula-

ted value, since the value of  $R$  for  $C_6H_6$  is determined from the study of  $R$  of benzene derivatives omitting benzene as it gives very different value for  $R$  ( $C_6H_6$ ).

TABLE III  
*Carbon tetrachloride in methyl alcohol.*  
Temp. = 30°.

$x$	$D$ .	$\eta \times 10^3$ .	$M_m$ .	$R_m$ .	$R_x$
0.0000	0.7903	4.90	32.00	50.30	—
0.0355	0.8863	5.40	36.33	53.13	129.7
0.1574	1.0640	5.94	51.25	63.10	130.5
0.2723	1.1720	6.65	65.21	71.94	129.8
0.4653	1.2830	7.10	86.50	90.26	129.6
0.6066	1.4380	7.60	106.08	98.28	129.4
0.7506	1.4790	7.66	122.18	108.64	129.5
0.9010	1.5430	7.80	141.98	121.90	129.7
1.0000	1.5740	7.96	154.00	—	129.7

Temp. = 40°.

0.0000	0.7823	4.90	32.00	50.01	—
0.0355	0.8655	5.40	36.33	52.90	129.7
0.1574	1.0440	5.94	51.25	65.52	130.5
0.2723	1.1620	6.65	65.21	71.28	129.8
0.4653	1.2790	7.10	86.50	86.37	129.6
0.6066	1.4169	7.60	106.08	97.71	129.4
0.7506	1.4520	7.66	122.18	108.29	129.5
0.9010	1.5364	7.80	141.98	120.56	129.7
1.0000	1.5650	7.96	154.00	—	129.7

Temp. = 50°.

0.0000	0.7747	4.16	32.00	49.74	—
0.0355	0.8569	5.10	36.33	51.97	126.9
0.1574	1.0320	5.43	51.25	61.32	125.9
0.2723	1.1593	6.12	65.21	70.52	127.4
0.4653	1.1990	6.42	86.50	91.05	126.6
0.6066	1.4010	6.82	106.08	96.16	127.2
0.7506	1.4460	6.98	122.18	107.71	126.9
0.9010	1.5255	7.06	141.98	119.00	127.2
1.0000	1.5360	7.12	154.00	—	127.9

Reale. (b.p.) = 142

In case of carbon tetrachloride dissolved in methyl alcohol also, the mixture law holds for all molar concentrations. The values of  $R_x$  are higher than the calculated value and fall with increase of temperature and approach the calculated value as the temperature increases. This is as expected as the value  $R_{calc.}$  is at the boiling point of the liquid. The deviation of  $R_x$  observed by us at lower temperature from  $R_{calc.}$  is much greater in this case than in the case of benzene-methyl alcohol mixture, because the value of  $R$  for pure  $CCl_4$  varies appreciably with temperature. Friend and Hargreave's results (*loc. cit.*, p. 644) will illustrate this.

TABLE IV

Temperature	...	60°	100°	180°
$R(CCl_4)$	...	126.0	125.1	124.2

TABLE V

*Chloroform in methyl alcohol.*

Temp. = 30°.

$x.$	$D.$	$\eta \times 10^3.$	$M_m.$	$R_m.$	$R_x.$
0.0000	0.7903	5.60	32.00	50.30	—
0.0499	0.8539	5.90	36.35	53.15	106.8
0.1326	1.0740	6.42	43.59	51.14	106.3
0.3228	1.1190	6.53	60.25	68.12	105.5
0.4234	1.1890	6.34	69.03	73.16	104.6
.5123	1.2370	6.21	76.83	77.62	103.4
0.6981	1.3440	6.08	93.07	86.80	102.6
0.8262	1.3960	6.10	104.28	93.67	102.8
1.0000	1.4590	6.10	119.50	—	102.9

Temp. = 40°.

0.0000	0.7823	4.90	32.00	50.01	—
0.0499	0.8441	5.27	36.35	52.88	105.7
0.1326	1.0610	5.57	43.59	50.89	105.2
0.3228	1.1090	5.66	60.25	67.50	103.9
0.4234	1.1690	5.54	69.03	72.98	104.1
0.5123	1.2290	5.49	76.83	77.29	103.4
0.6981	1.3290	5.45	93.07	86.56	102.3
0.8262	1.3750	5.50	104.28	93.57	102.8
1.0000	1.4440	5.57	119.50	—	102.8



TABLE V (contd.)

Temp. = 50°.

$x$ .	$D$ .	$\eta \times 10^3$	$M_m$ .	$R_m$ .	$R_x$ .
0.0000	0.7747	4.16	32.00	49.71	—
0.0499	0.8337	4.39	36.35	52.46	105.0
0.1326	1.1040	4.48	43.59	50.54	104.9
0.3228	1.1083	4.51	60.25	67.14	103.7
0.4234	1.1570	4.68	69.03	72.34	103.6
0.5123	1.2270	4.74	76.83	76.09	102.8
0.6981	1.3130	4.82	93.07	86.26	102.7
0.8262	1.3690	4.96	104.28	93.09	102.3
1.0000	1.4240	4.91	119.50	—	102.3

 $R_{calc.} (b.p.) = 100.2$ 

TABLE VI

*Toluene in methyl alcohol.*

Temp. = 30°.

$x$ .	$D$ .	$\eta \times 10^3$ .	$M_m$ .	$R_m$ .	$R_x$ .
0.0000	0.7903	5.60	32.00	50.30	—
0.0724	0.8044	5.88	36.35	60.26	134.4
0.1636	0.8179	5.88	41.84	63.84	133.0
0.3517	0.8307	5.69	53.15	79.05	133.3
0.5095	0.8392	5.44	62.66	92.26	132.6
0.6126	0.8447	5.39	68.85	100.61	132.4
0.7321	0.8494	5.32	76.04	110.27	132.3
0.8541	0.8551	5.27	83.12	119.50	132.0
1.0000	0.8586	5.38	92.14	—	132.4

Temp. = 40°.

0.0000	0.7823	4.90	32.00	50.01	—
0.0724	0.7938	5.00	36.35	59.84	131.5
0.1636	0.8050	5.03	41.84	63.59	132.4
0.3517	0.8221	4.87	53.15	78.79	131.7
0.5095	0.8303	4.85	62.66	91.94	132.2
0.6126	0.8351	4.80	68.85	100.03	131.6
0.7321	0.8422	4.75	76.04	109.70	131.5
0.8541	0.8437	4.64	83.12	119.50	131.4
1.0000	0.8498	4.81	92.14	—	131.9

TABLE VI (contd.)

Temp. = 50°.

$x$ .	$D$ .	$\eta \times 10^3$ .	$M_m$ .	$R_m$ .	$R_x$ .
0.0000	0.7747	4.16	32.00	49.71	—
0.0724	0.7859	4.33	36.35	59.30	130.2
0.1636	0.7962	4.41	41.84	63.27	129.7
0.3517	0.8127	4.07	53.15	77.82	130.5
0.5095	0.8215	4.20	62.66	91.28	131.2
0.6126	0.8239	4.13	68.85	99.76	131.4
0.7321	0.8283	4.10	76.04	109.45	131.3
0.8541	0.8377	4.08	83.12	118.20	130.3
1.0000	0.8403	4.24	92.14	—	131.4

 $R_{calc.} (b.p.) = 130$ 

The results obtained for  $\text{CHCl}_3$  and  $\text{CCl}_4$  in methyl alcohol are similar. The value of  $R_x$  falls with temperature as expected. In case of  $\text{CHCl}_3$ , however, at lower concentrations the value of  $R_x$  deviates rather appreciably, but for higher concentrations the deviation is not appreciable. The high results at lower concentrations or for dilute solutions have been obtained at all the three temperatures, although the variation is much less at higher temperatures. Toluene, however, does not show this discrepancy. Thus, it may be stated that the mixture law is applicable for non-associated liquids in associated solvent, methyl alcohol.

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BEHAVIOUR OF NITROPHENOLS WITH *p*-TOLUENE SULPHONYL  
CHLORIDE. PART V. ABNORMAL BEHAVIOUR OF SOME  
DINITROPHENOLS WITH METHYL GROUP IN  
THE *META* POSITION

BY SHIAM SUNDER JOSHI AND BANKY BEHARI LAL KAPOOR

Behaviour of 4-bromo-3-methyl-2,6-dinitrophenol, 3,5-dimethyl-2,4-dinitrophenol and 4-chloro-3,5-dimethyl-2,6-dinitrophenol has been studied. They are all found to form *p*-toluene sulphonic acid esters in sodium carbonate solution

Abnormal behaviour of some dinitrophenols has been observed by several workers (Ullmann and co-workers, *Ber.*, 1908, **41**, 1870; 1911, **44**, 3731; Sane and Joshi, *J. Chem. Soc.*, 1924, 2481; *J. Indian Chem. Soc.*, 1928, **5**, 299; 1932, **9**, 59; Sen, *ibid.*, 1946, **23**, 53). One of such an abnormality manifests itself in the replacement of the hydroxyl group by a chlorine atom when heated with *p*-toluenesulphonyl chloride and diethylaniline in the case of those nitrophenols in which the nitro groups are either in the *ortho* positions or in the *ortho* and *para* positions to the hydroxyl group. By heating these nitrophenols with the acid chloride and an aqueous solution of sodium carbonate, *p*-toluene sulphonic esters are obtained. If these nitrophenols have a chlorine atom in the *meta* position, it shows hardly any effect in their behaviour, but a methyl group in the *meta* position exerts in some cases a marked influence. In a few cases the hydroxyl group is replaced by chlorine, whilst in others it is not so. They are, however, readily converted into their sulphonic acid esters.

The behaviour of these esters towards ammonia, aniline, etc. is not similar. The esters of all those dinitrophenols in which the hydroxyl is replaced by chlorine are found to be reactive,  $-OSO_2C_6H_5$  group being replaced by  $-NH_2$ ,  $-NHPh$ , etc. group. The esters of those nitrophenols that have a methyl group in the *meta* position do not behave in one way. Some esters such as those of 4:6-dinitro-*m*-cresol and 2-iodo-4:6-dinitro-*m*-cresol are reactive, whereas others such as those of 4-chloro-2:6-dinitro-*m*-cresol and 3:6-dimethyl-2:4-dinitrophenol are unreactive under similar conditions.

In the present communication the behaviour of 4-bromo-3-methyl-2,6-dinitrophenol, 3,5-dimethyl-2,4-dinitrophenol and 4-chloro-3,5-dimethyl-2,6-dinitrophenol has been studied. They all form *p*-toluene sulphonic esters in sodium carbonate solution. The first one forms only the sulphonic acid ester when heated with the acid chloride and diethylaniline, whilst the last two do not form even an ester under similar conditions. In none of these cases the hydroxyl is replaced by chlorine. All these esters are quite stable and unreactive towards ammonia and aniline.

EXPERIMENTAL

**3:5-Dimethyl-2:4-dinitrophenol.**—To a mixture of sulphuric acid (34 c.c., *d* 1.58) and nitric acid (24 c.c., *d* 1.33) was added 3:5-dimethylphenol (10 g.) in small quanti-

ties with vigorous stirring. The product was then heated on a water-bath with occasional shaking till all the nitrous fumes were removed. It was then cooled, filtered, washed with hot water and crystallised from 75% acetic acid, when light yellow crystals were obtained, m.p.  $106^{\circ}$ ; it is insoluble in water, slightly soluble in alcohol and easily soluble in acetic acid. The white crystals of its acetate melt at  $148^{\circ}$  and of benzoate, prepared with benzoyl chloride in presence of either pyridine or sodium acetate, melt at  $156^{\circ}$ .

Under similar conditions 4-chloro-3:5-dimethylphenol yielded on nitration yellow crystals of 4-chloro-3:5-dimethyl-2:6-dinitrophenol, turning scarlet-red on heating and melting with swelling at  $180^{\circ}$  and dissolving in solvents as in the above compound. The white crystals of its acetate melt at  $108^{\circ}$  and of benzoate, at  $125^{\circ}$ .

**4-Bromo-3-methyl-2:6-dinitrophenyl-*p*-toluene Sulphonate.**—*p*-Toluenesulphonyl chloride (2.4 g.) and sodium carbonate (3 g.) were added to a boiling mixture of 4-bromo-2:6-dinitro-*m*-cresol (3 g.) and water (10 c.c.) in small quantities with vigorous shaking. When the smell of the acid chloride had disappeared, a solid was separated by filtration. It was washed with hot sodium carbonate solution and crystallised from a mixture of alcohol and acetone, m.p.  $158^{\circ}$ . It is slightly soluble in alcohol and more so in acetone. (Found: S, 7.02.  $C_{14}H_{11}O_7N_2BrS$  requires S, 7.42 per cent). The same ester was obtained by heating the substituted cresol with *p*-toluenesulphonyl chloride and diethylaniline on a water-bath for 4 hours.

Under similar conditions 3:5-dimethyl-2:4-dinitrophenol yielded 3:5-dimethyl-2:6-dinitrophenyl-*p*-toluene sulphonate, m.p.  $171^{\circ}$  (Found: S, 9.12.  $C_{15}H_{14}O_7N_2S$  requires S, 8.74 per cent) and 4-chloro-3:5-dimethyl-2:6-dinitrophenyl-*p*-toluene sulphonate, m.p.  $199^{\circ}$  (Found: S, 7.71.  $C_{15}H_{13}O_7N_2SCl$  requires S, 8.0 per cent) having similar solubilities. From these two substituted xylenols, neither an ester nor a chloro compound was obtained when they were heated with *p*-toluenesulphonyl chloride and diethylaniline.

# STUDIES OF NITRO-*m*-CRESOLS AND THEIR HALOGEN DERIVATIVES. PART I. 6-BROMO-2:4-DINITRO- AND 4-BROMO-2:4-DINITRO-*m*-CRESOLS

BY SHIAM SUNDER JOSHI AND SATYA PRAKASH GUPTA

6-Bromo-2:4-dinitro-*m*-cresol and 4-bromo-2:6-dinitro-*m*-cresol have been prepared and their constitution confirmed.

The melting point of 6-bromo-2:4-dinitro-*m*-cresol as given in literature (Kehrmann, and Rust, *Annalen*, 1898, **303**, 29; Gibbs and Robertson, *J. Chem. Soc.*, 1914, **108**, 1891; Raiford and Leavell, *J. Amer. Chem. Soc.*, 1914, **36**, 1498) is 115°, whereas we have found it to be 106°. The melting point of 4-bromo-2:6-dinitro-*m*-cresol as found by us is nearly the same as that given in literature. Of the three bromodinitro-*m*-cresols, Sane and Joshi (*J. Indian Chem. Soc.*, 1928, **5**, 299) have shown that 2-bromo-4:6-dinitro-*m*-cresol melts at 115°. On bromination and subsequent nitration of *m*-cresol two monobromodinitro-*m*-cresols have been obtained by us, one melting at 106° and the other at 78°. The latter has also been obtained by brominating 6-nitro-*m*-cresol and subsequent nitration of 4-bromo-6-nitro-*m*-cresol so obtained, which proves its constitution to be 4-bromo-2:6-dinitro-*m*-cresol. The constitution of the other bromodinitro-*m*-cresol melting at 106° is consequently 6-bromo-2:4-dinitro-*m*-cresol. The three bromodinitro-*m*-cresols have the following characteristics (Table I).

TABLE I

Compound.	M. p.	Colour.	Solubility.	Acetyl, m.p.
4-Bromo-2:6-dinitro- <i>m</i> -cresol	78°	Colorless, pale yellow when moist	More in alcohol, less in acetic acid	96°
6-Bromo-2:4-dinitro- <i>m</i> -cresol	106°	Orange	Less in alcohol, more in acetic acid	81°
2-Bromo-4:6-dinitro- <i>m</i> -cresol	115°	Light brown	----	85-86°

## EXPERIMENTAL

**6-Bromo-2:4-dinitro-*m*-cresol.**—*m*-Cresol (108 g.), dissolved in acetic acid (100 c.c.), was treated with bromine (160 g.) dissolved in acetic acid (200 g.). The mixture was well shaken and cooled during the addition and washed rapidly with water to remove hydrobromic acid. The insoluble liquid so obtained was mixed with strong H<sub>2</sub>SO<sub>4</sub> (400 c.c., *d* 1.58), cooled and treated with HNO<sub>3</sub> (200 c.c., *d* 1.34) dropwise with vigorous shaking and the temperature was not allowed to rise above 40°. After standing overnight, it was heated on a water-bath till nitrous fumes ceased to evolve. On treatment with water a semi-solid, dark red product separated out. On crystallisation from alcohol it gave orange-yellow crystals (80-90 g.), m.p. 106°. (Found: Br, 28.39. C<sub>7</sub>H<sub>5</sub>O<sub>5</sub>N<sub>2</sub>Br

requires Br, 28.88 per cent). On acetylation it gives an acetate, m.p.  $81^{\circ}$  and on benzoylation, a benzoate, m.p.  $103^{\circ}$

*4-Bromo-2:6-dinitro-m-cresol.*—(i). The alcoholic filtrate from above on treating with water gave a thick reddish brown liquid which on crystallisation from acetic acid yielded white leaflets (20-30 g.), m.p.  $78^{\circ}$ . (Found : Br, 28.49.  $C_7H_5O_5N_2Br$  requires Br, 28.88 per cent). On acetylation it yields an acetate, m.p.  $96^{\circ}$  and on benzoylation, a benzoate, m.p.  $121^{\circ}$ .

The same products were obtained when bromo-*m*-cresols were nitrated at  $5^{\circ}$ - $10^{\circ}$  except that the relative proportion of the yield of the two products was reversed.

(ii). 6-Nitro-*m*-cresol (5 g.), dissolved in acetic acid (5 c.c.), was treated dropwise with vigorous shaking with bromine (5.2 g.), dissolved in acetic acid (10 c.c.) and of 4-bromo-6-nitro-*m*-cresol (6.5 g.) so obtained, 2 g. of it were dissolved in acetic acid and treated with a mixture of  $HNO_3$  (5 c.c.,  $d$  1.34) and  $H_2SO_4$  (8 c.c.,  $d$  1.58) with vigorous shaking and then treated as mentioned above when crystals (2 g.) from acetic acid of m.p.  $78^{\circ}$  were obtained.

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## REVIEWS

**Organic Analytical Reagents.**—By Frank J. Welcher, Ph.D., Associate Professor of Chemistry, Extension Division. Published by D. Van Nostrand Company, Inc., New York. Pp. 593.

The book under review constitutes the 3rd volume of "Organic Analytical Reagents" by the author. The informations collected in this volume relate to the reagents that have not been dealt with in the two previous ones, viz. Vol. I and Vol. II. The reagents discussed in this volume have been arranged in three parts. Part I describes the use of Heterocyclic Nitrogen Compounds. Part II deals with the use of the Oximes and Part III with that of acidic imino-compounds.

As in the two other volumes, the reader will find a more or less complete reference to literature up to 1945 for every reagent discussed and that methods have also been included for the preparation of these reagents.

The author has done a great service to the advanced students and workers in analytical chemistry by collecting in one place all informations relating to the analytical use of any given reagent.

The book should find a place in every analytical research laboratory.

P. R.

**Modern Synthetic Rubbers.**—By Harry Barron. Published by Chapman and Hall, London, pp. 636+xx. Price 45/sh.

Synthetic Rubber is a fascinating subject. Harry Barron's "Modern Synthetic Rubbers" is indeed a fascinating book to readers interested in the subject. Three editions and reprinting once during six years indicate undisputedly the popularity of the book among its readers. The general scheme and lay-out of this edition are more or less similar to its predecessors. The author has helped himself in enlarging and revising the book from a mass of details released by the lifting of the iron curtain of war-time secrecy of the tremendous advances made in the technology of synthetic rubbers and elastomers and also from data embodied in the Combined Service Intelligence Reports on German industry. Main additions have been made in the book by including a section on "Compounding" in Chapter XI (Part II) and a number of tables in chapter VII dealing with the raw materials-petroleum. The statistical tables dealing with production, consumption, price, export of raw materials and finished products, have been made up to date.

The get-up and printing of the book bear the hall mark of perfection of the reputed publishers.

G. B.

**The Royal Institution.**—By Thomson Martin. Published for the British Council by Longmans, Green & Co., London.

History is and must always largely be the story of the great ones who have guided and influenced the activities of their fellow men. The same is true also of the Institu-

tions. Many of the British Institutions are to the Britishers to-day what the acknowledged and elected leaders of men have made them. It is the traditional British way *to retain the ancient forms, to compromise with the past, to adapt constitutions to fit them to new work and new conditions, but not to discard them.* The British scientific Institutions, and among them the Royal Institution, are no exception to this rule.

According to the author, the Royal Institution, to most of the Britishers, is a place synonymous to where Faraday lived and worked. Among British scientific institutions, none has a more interesting history or a more remarkable record of achievement than the Royal Institution. Founded by an American, Benjamin Thompson, Count Rumford, it early attracted men of genius. One of the greatest of them, Humphry Davy, set the example of combining scientific experiment with popular exposition; and it is this combination which for a hundred and fifty years has given to the Institution its unique character. Its house in London soon became, and has remained, one of the principal centres of research and meeting places of the scientific, and learned world. In more recent years other famous men, among them John Tyndall, James Dewar and William Bragg, have carried on the work and sustained the high tradition of the Institution. And out of devotion and respect to these leaders of science and men, who have made this Institution a 'Mecca' in the scientific world, the Secretary of the Institution, Mr. Martin, has devoted 52 pages in depicting their dynamic life stories.

G. B.

**Department of Research Report, Travancore University.** Pages 594 + xii.

The report published for first time contains record of the activities of the Department of Research of the Travancore University for the first seven years (1939-1946). It is a novel report of its kind and is intended to serve not only as a register of various types of work carried out but also as a basis of review on which future developments may be chalked out. The report has been ably compiled from accounts of work carried out in various research departments viz., Central Research Institute, Applied Botany, Applied Chemistry, Marine Biology and Fisheries, Observatory, Preventive Medicines, Statistical and other institutions. The report has been broadly divided into two sections. The first section records the activities of the various departments exclusive to the University and the second section contains reports of the activities of the various departments of H. E. the Maharaja's University College, the Textile Institute and of the College of Engineering. The report contains in addition ten appendices and 15 illustrations. The volume and nature of work carried out in various departments in the first seven years of its existence will do credit to any university in India.

G. B.



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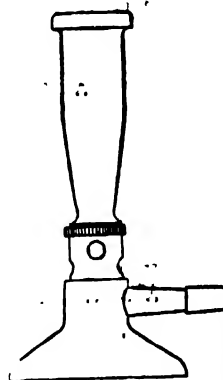
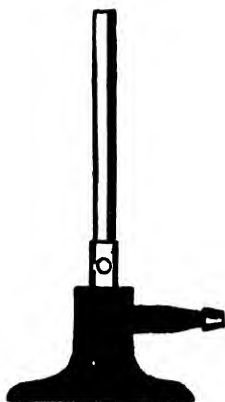
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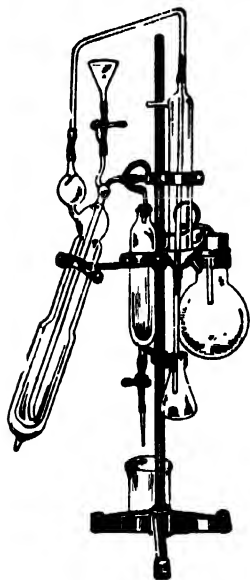
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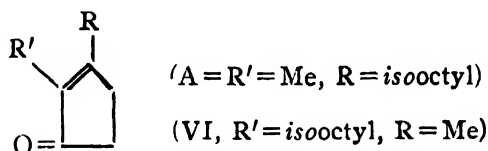


# SYNTHESIS OF ISOOCTYLMETHYLCYCLOPENTADIENE

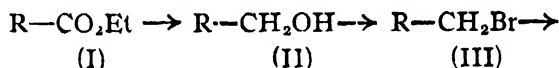
By PROVAS KUMAR DUTTA

A synthesis of 2-(methylheptyl)-3-methyl- $\Delta^2$ -cyclopentadiene has been described.

Attention was directed to the synthesis of certain methylcyclopentenones with the isooctyl side-chain attached to the carbon atom adjacent to that carrying the methyl group, of which the two following were the two (VI, A) immediate objectives.



Earlier attempts to synthesise this ketone (A) through the oxidation of the corresponding cyclopentene with selenium dioxide failed (Rydon, *J. Chem. Soc.*, 1940, 1546) and preliminary studies to build up similar cyclopentenone derivatives from 1:4-diketones have proved futile (Mitter and Dutta, this *Journal*, 1948, 25, 306). Experiments were next undertaken to synthesise (VI) according to the interesting method which has been recently developed for the preparation of substituted cyclopentenones through distillation of  $\gamma$ -lactones with phosphorus pentoxide (Frank *et al.*, *J. Amer. Chem. Soc.*, 1944, 66, 4).

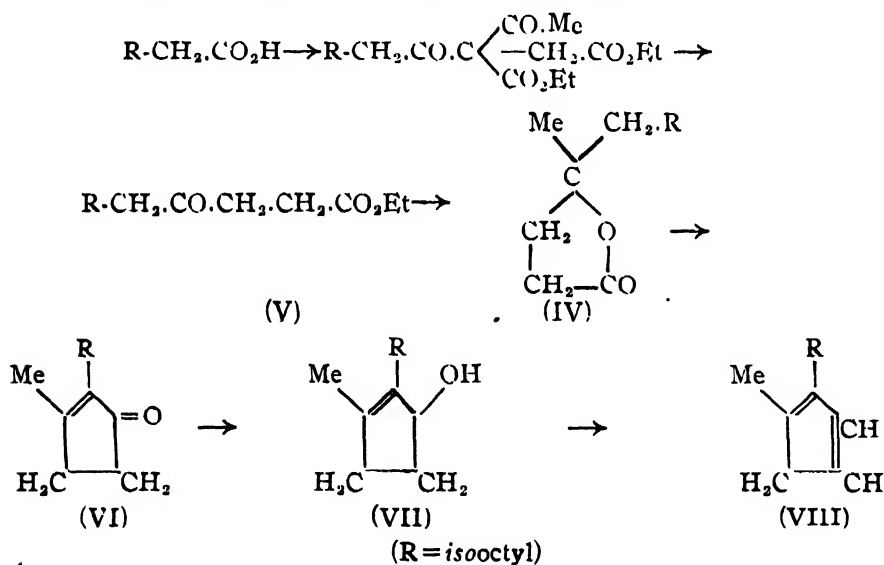


*sec*-isooctyl iodide is converted into cyanide which passes into the ester (I) directly on treatment with alcohol and sulphuric acid. Reduction of this ester with alcohol and sodium gives (II) which passes into the bromide (III) on refluxing with sulphuric and hydrobromic acids. The Grignard's complex, prepared from this bromide in presence of equivalent amount of methyl iodide, reacts smoothly with ethyl laevulinate in dilute ethereal solution in the cold. From the reaction mixture the lactone (IV) is obtained in rather a poor yield. The synthesis of the lactone has been carried out more successfully by employing the well known method developed by G. M. Robinson for the synthesis of long-chain keto-acids. The starting material in this case is *sec*-isooctyl-acetic acid (Dutta, this *Journal*, 1942, 19, 78). The acid chloride condenses smoothly with the sodio-salt of ethyl acetosuccinate. The crude condensation product is hydrolysed through prolonged shaking at the ordinary temperature (Chuang *et al.*, *Ber.*, 1936, 69, 1492). The keto-acid is isolated as its ethyl ester (V) which reacts smoothly with methylmagnesium iodide. The desired lactone (IV) is obtained in a good yield on hydrolysis with alkali and subsequent lactonisation on warming with dilute sulphuric acid. On distillation of the lactone over phosphorus pentoxide, the cyclopentenone

derivative (VI) is obtained in a moderate yield. The structure of the unsaturated *cyclopentenone* (VI) has been assigned on the basis of similar observations on the synthesis of dihydrojasnone from the lactone prepared from *isohexyl iodide* and *ethyl laevulinate* (Frank *et al.*, *loc. cit.* Dutta and Sen Gupta, this *Journal*, 1948, **28**, 213), and also from the later observations of Frank *et al.* (*J. Amer. Chem. Soc.*, 1948, **60**, 1379) where it has been definitely established that in the case of  $\gamma$ -lactones having a methylene group and a methyl group available for the formation of the *cyclopentenone* ring, the reaction always proceeds in the direction where only the methylene group is involved.

Reduction of the ketone with aluminium *isopropoxide* affords the unsaturated alcohol (VII). This is converted into the chloride with thionyl chloride in presence of pyridine and the chloro compound is heated with excess of dimethylaniline to give the doubly unsaturated compound (VIII). Attempts to introduce different groups at the methylene group through the potassium salt of the *cyclopentadiene* (VIII) have met with failure so far.

The whole scheme of work can be drawn up as follows:—



#### EXPERIMENTAL

**Ethyl 2:6-Dimethylheptoate (I).**—A mixture consisting of methylheptyl cyanide (34 g.), rectified spirit (47 c.c.), alcohol (47 c.c.) and concentrated sulphuric acid (39 c.c.) was heated under reflux for 12 hours in an oil-bath. The resulting ester was cooled, diluted with water and extracted with ether. A mobile liquid passed over at 80°-85°/12 mm. having a sweet smell, yield 25 g. (Found: C, 71.6; H, 11.4.  $\text{C}_{12}\text{H}_{24}\text{O}_2$  requires C, 72.0; H, 12.0 per cent).

**2:6-Dimethylheptyl Alcohol (II).**—Sodium (21 g.) was placed in a three-necked flask and the above ester (25 g.) and alcohol, dried over magnesium methoxide, were next introduced. After the vigorous reaction had subsided, it was refluxed in an oil-bath until the whole of sodium had reacted. It was cooled, diluted considerably with

water and extracted with ether. On working up in the usual way the desired alcohol (13 g.) passed over at  $90^{\circ}$ - $95^{\circ}$ /18 mm.

**2,6-Dimethylheptyl Bromide (III).**—A mixture of 2:6-dimethylheptyl alcohol (13 g.), hydrobromic acid (48%, 45 g.) and concentrated sulphuric acid (11.5 g., d 1.84) was boiled under reflux for 2 hours. It was diluted with water and the bromide layer separated, and washed with a little cold concentrated sulphuric acid to remove the unchanged alcohol. The bromide (12 g.) was collected at  $85^{\circ}$ /18 mm. as a heavy liquid.

**Lactone of  $\delta$ -(2:6-Dimethylhexyl)- $\gamma$ -methyl- $\gamma$ -hydroxyvaleric Acid (IV).**—Magnesium (4 g.) was covered with ether (20 c.c.) and methyl iodide (2 c.c.) was added to start the reaction. Next it was warmed and to the hot solution the above bromide (6 g.) in ether (25 c.c.) was slowly added. The mixture was refluxed gently for some time more until there was no perceptible reaction. Ethyl laevulinate (8 g.), dissolved in ether (50 c.c.), was cooled in an ice-bath and to this the above Grignard's complex was added gradually with shaking. It was allowed to stand for further one hour in the ice-bath and at ordinary temperature for another half-an-hour. The product was then decomposed with ice and hydrochloric acid and isolated by means of ether; it was dried ( $\text{Na}_2\text{SO}_4$ ), ether removed and the residual liquid distilled in *vacuo*. The unchanged bromide and the ethyl laevulinate were collected as a forerun and the desired lactone in a poor yield at  $135^{\circ}$ - $140^{\circ}$ /6 mm., yield 1.5 g. (Found: C, 73.8; H, 11.02.  $\text{C}_{14}\text{H}_{26}\text{O}_2$  requires C, 74.4; H, 11.5 per cent).

**Methylheptylacetic Acid.**—Methylheptyl iodide (45 g.) was condensed with ethyl malonate (45 g.) in presence of sodium (4.5 g.) in alcohol (80 c.c.) in the usual way. It was worked up and the desired ester was obtained (b.p.  $128^{\circ}$ /4 mm.), yield 39 g. It was hydrolysed by refluxing the ester (25 g.) with caustic potash (15 g.) in water (15 c.c.) and rectified spirit (60 c.c.) for 6 hours. Alcohol was removed (water-bath) and the dibasic acid was obtained on acidification and subsequent extraction with ether. The residue left after the removal of the solvent was heated (oil-bath,  $180^{\circ}$ - $190^{\circ}$ ) for half-an-hour when decarboxylation was complete. The acid was isolated by vacuum distillation, b.p.  $136^{\circ}$ /13 mm., yield 15 g.

**Methylheptylacetyl Chloride.**—Methylheptylacetic acid (46 g.) was mixed with phosphorus trichloride (12 c.c.) and the resulting mixture was left overnight. Next it was heated on the water-bath for 2 hours. The clear upper layer was decanted off and distilled, when the acid chloride passed over at  $90^{\circ}$ - $100^{\circ}$ /14 mm., yield 46 g.

**Condensation of Ethyl Acetosuccinate and Methylheptylacetyl Chloride: Ethyl  $\delta$ -Methylheptyl- $\gamma$ -ketovalerate (V)**—Sodium (6.2 g.) was molecularised and was taken under ether. This was cooled in ice and ethyl acetosuccinate (58 g.) was added dropwise. The mixture was kept overnight when a clear solution was obtained. Next day it was again cooled in ice and the acid chloride (46 g.) was added dropwise with occasional shaking. When the addition was complete, the mixture was refluxed (water-bath) for 2 hours. There was very little separation of sodium chloride. It was cooled and extracted with ether. The solvent was removed and it was directly employed for the next operation. The crude condensation product (100 g.), obtained from the previous reaction, was shaken with a mixture of distilled water (1800 c.c.), caustic potash (76 g.) and rectified spirit (900 c.c.) for 30 hours in a mechanical shaker. The turbid solution thus produced was neutralised with  $\text{H}_2\text{SO}_4$  (75 g.) and then evaporated

on the water-bath to remove alcohol. The residue was then strongly acidified and extracted with ether. After removal of ether, the remaining liquid was again hydrolysed by refluxing with caustic soda solution (660 c.c., 2*N*) on a water-bath for 3 hours. The solution was again acidified and extracted with ether. The residue after removal of ether was heated (water-bath) for half-an-hour. It was dried in *vacuo* and esterified with a cooled mixture of alcohol (150 c.c.) and concentrated sulphuric (9 c.c.) for 15 hours. The ester (25 g.) was isolated in the usual manner, b.p. 130°-132°/3 mm. (Found: C, 69.7; H, 10.84.  $C_{15}H_{26}O_3$  requires C, 70.3; H, 10.94 per cent).

*δ-Methylheptyl-γ-methyl-γ-valerolactone* (IV).—Grignard's complex, prepared from magnesium (3.5 g.) and methyl iodide (15 c.c.), was added to the above keto-ester (25 g.) in dry ether (150 c.c.), cooled in a freezing mixture. The reaction mixture was allowed to stand for 2 hours and then decomposed with ice and ammonium chloride, acidified and extracted with ether. The residue after removal of the solvent was heated with alcoholic caustic potash solution (100 c.c., 10%) on the water-bath for 1 hour. The alcohol was removed and the ethereal extract of the alkaline solution containing the neutral fraction, if any, was rejected. The main alkaline layer was acidified and the mixture refluxed for 1 hour with dilute sulphuric acid (100 c.c., 10%). Finally it was extracted (ether), the ethereal extract washed with sodium bicarbonate solution and worked up as usual. A viscous liquid (18 g.) boiled at 125°-130°/3 mm. (Found: C, 74.4; H, 11.5.  $C_{14}H_{26}O_2$  requires C, 74.3; H, 11.5 per cent).

*2-Methylheptyl-3-methyl-Δ<sup>2</sup>-cyclopenten-1-one* (VI).—The above lactone (8 g.) was mixed with  $P_2O_5$  (4 g.) in a Claisen flask and heated in *vacuo* (oil-bath, 140°-150°) when a vigorous reaction took place and the whole mass turned dark brown. A mobile liquid (3 g.) passed over at 126°-134°/11 mm. On redistillation it came over at 126°-130°/11 mm. It has a characteristic smell. (Found: C, 79.9; H, 11.8.  $C_{14}H_{24}O$  requires C, 80.5; H, 11.6 per cent).

*2-Methylheptyl-3-methyl-Δ<sup>2</sup>-cyclopenten-1-ol* (VII).—The above ketone (5 g.) was reduced with aluminium isopropylate, prepared from aluminium (3 g.) in isopropyl alcohol (60 c.c.) in the usual way. During distillation further isopropyl alcohol (40 c.c.) was added. The temperature of the oil-bath was kept at 90°-110°. On working up in the usual way the unsaturated alcohol was obtained boiling at 122°-124°/7 mm. having rather an unpleasant odour, yield 3.5 g. (Found: C, 79.8; H, 11.9.  $C_{14}H_{26}O$  requires C, 80.0; H, 12.1 per cent). Attempts to prepare a phenylurethane derivative failed.

*2-Methylheptyl-3-methyl-Δ<sup>2,5</sup>-cyclopentadiene* (VIII).—The above alcohol (3 g.) was dissolved in freshly distilled dimethylaniline (8 c.c.) and cooled. To this was added thionyl chloride (2 c.c.) when the mass turned deep brown. Next, excess thionyl chloride was removed in a high vacuum and the residue was heated in an oil-bath at 180°-190° for half-an-hour. On working up the diene was obtained as a clear, colorless oil boiling at 92°/2 mm., yield 1.2 g. (Found: C, 86.6; H, 12.1.  $C_{14}H_{24}$  requires C, 87.5; H, 12.5 per cent).

The author's thanks are due to Dr. P. C. Dutta for his valuable help in this piece of investigation.



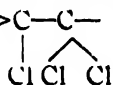
## SYNTHETIC INSECTICIDES. PART I. SYNTHESIS OF $\alpha\alpha$ -BIS-(ARYL)- $\beta\beta\gamma$ -TRICHLORO-*n*-BUTANES

By (MISS) LATIKA H. DALAL AND R. C. SHAH

In the present work the condensations of benzene, chlorobenzene, bromobenzene and naphthalene with butylchloral hydrate have been carried out when in the first three cases the products of the type  $\alpha\alpha$ -bis-(R-pnenyl)- $\beta\beta\gamma$ -trichloro-*n* butanes (where R=H, Cl and Br respectively) were obtained. The structures of these compounds have been established by first dehydrohalogenating and subsequently oxidising the crude dehydrohalogenated compounds to their respective benzophenones. Dehydrohalogenation and oxidation of the naphthalene condensation product were attempted but without success. Hence, this compound has been provisionally assigned the constitution  $\alpha\alpha$ -bis-( $\alpha$ -naphthyl)- $\beta\beta\gamma$ -trichloro-*n*-butane.

The discovery by Lauger Muller and Martin (*Helv. Chim. Acta*, 1944, 27, 897) of the remarkable insecticidal properties of the compound  $\alpha\alpha$ -bis-(*p*-chlorophenyl)- $\beta\beta\beta$ -trichloroethane, popularly known as DDT, has opened a wide field of research in synthetic insecticides. Since then, much work on the synthesis of the analogues of DDT has been carried out with a view to obtaining compounds of possible insecticidal action. Stephenson and Waters (*J. Chem. Soc.*, 1946, 339) have synthesised a number of 4:4'-disubstituted derivatives of  $\alpha\alpha$ -(diphenyl)- $\beta\beta\beta$ -trichloroethane (DT), like 4:4'-dimethyl-DT, 4:4'-diethyl-DT, 4:4'-dibromo-DT, 4:4'-difluoro-DT, 4:4'-dihydroxy-DT and their methyl, ethyl, propyl, butyl ethers, etc. So also the bromal analogues of DDT like  $\alpha\alpha$ -bis-(*p*-chlorophenyl)- $\beta\beta\beta$ -tribromoethane and  $\alpha\alpha$ -bis-(*p*-bromophenyl)- $\beta\beta\beta$ -tribromoethane have been synthesised by Cristol and Haller (*J. Amer. Chem. Soc.*, 1946, 68, 140) and Lauger *et al.* (*loc. cit.*)

Lauger and co-workers (*loc. cit.*) in their study of insecticidal property and chemical constitution observed that  $\alpha\alpha$ -bis-(*p*-chlorophenyl)- $\alpha\beta\beta$ -trichloroethane with the grouping



to synthesise compounds by using other halogenated aldehyde instead of chloral so that

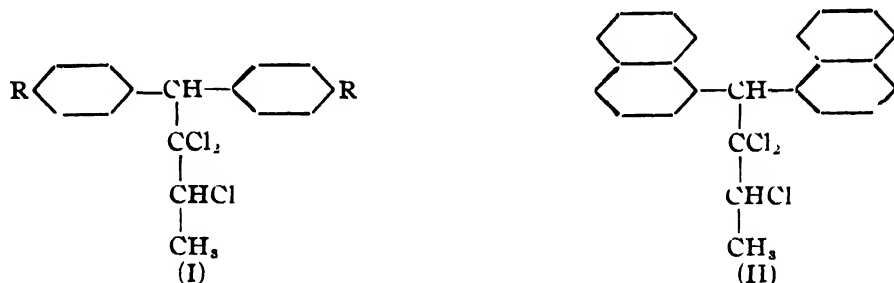
the grouping  $>CH-C \begin{array}{l} \diagup Cl \\ | \\ Cl \end{array}$  present in DDT be replaced by  $-C \begin{array}{l} | \\ Cl \\ | \quad \diagup \\ Cl \quad Cl \end{array} -C$ . For this

purpose butylchloral hydrate was selected so that the condensation products obtained

would have the grouping  $CH_3-C \begin{array}{l} H \\ | \\ Cl \quad \diagup \\ Cl \quad Cl \end{array} -C \begin{array}{l} \diagup \\ | \\ Cl \end{array} -CH$ , and which may possess insecticidal activity.

Reference to literature reveals that so far no work on the condensation of butylchloral hydrate with hydrocarbons and halohydrocarbons has been carried out.

In the present work butylchloral hydrate has been condensed with benzene, naphthalene, chlorobenzene and bromobenzene. Butylchloral hydrate, when condensed with chlorobenzene in presence of oleum at 29°-30°, gave  $\alpha\alpha$ -bis-(*p*-chlorophenyl)- $\beta\beta\gamma$ -trichloro-*n*-butane (I, R=Cl). The same compound was obtained with chlorosulphonic acid; however, oleum was found to be a better condensing agent. The structure of this compound was proved by dehydrohalogenation and subsequent oxidation of the crude unsaturated compound, when *pp'*-dichlorobenzophenone was obtained.



Similarly, the condensations of benzene and bromobenzene with butylchloral hydrate were carried out when  $\alpha\alpha$ -bis-(phenyl)- $\beta\beta\gamma$ -trichloro-*n*-butane (I, R=H) and  $\alpha\alpha$ -bis-(*p*-bromophenyl)- $\beta\beta\gamma$ -trichloro-*n*-butane (I, R=Br) respectively were obtained. The structures of these compounds were established in the same way, by degradation through dehydrohalogenation and subsequent oxidation to the respective benzophenones.

Naphthalene, when similarly condensed with butylchloral hydrate, gave a di-condensation product (m.p. 196-98°). All attempts at dehydrohalogenating this compound proved unsuccessful. It may be tentatively suggested that the constitution of the compound is  $\alpha\alpha$ -bis-( $\alpha$ -naphthyl)- $\beta\beta\gamma$ -trichloro-*n*-butane (II). The dehydrohalogenation may not be taking place due to steric hindrance exerted by the heavy groups (fused benzene rings) attached on both the sides in position *ortho* to the carbon atoms which are linked to the butylchloral group.

Further work on similar condensations with alkylbenzenes, chloronaphthalenes, phenols and their ethers, etc., is in progress.

#### EXPERIMENTAL

**Condensation of Butylchloral Hydrate with Chlorobenzene:**  $\alpha\alpha$ -bis-(*p*-Chlorophenyl)- $\beta\beta\gamma$ -trichloro-*n*-butane.—Butylchloral hydrate (30 g.) was taken in a three-necked flask equipped with a mercury seal stirrer, thermometer and a separating funnel which contained oleum (5%, 100 g.). About 10 g. of oleum (24%) were added to butylchloral hydrate with stirring to remove water of the hydrate, indication being no lowering of temperature even if more oleum were added. It was then allowed to attain room temperature (29°-31°) and chlorobenzene (38.5 g.) was added followed by a slow addition of oleum with stirring, controlling the temperature at 29°-31°, by external cooling. The stirring was continued for 5 hours in all. The reaction mixture was kept overnight and next day it was poured over crushed ice when yellowish brown pasty product was obtained. This was washed well with cold and then boiling water.

After two crystallisations from acetic acid needles were obtained, m.p.  $81^{\circ}$ , yield 10 g. (Found: Cl, 46.3.  $C_{16}H_{13}Cl_5$  requires Cl, 46.3 per cent). *Tetranitro derivative*, m.p.  $241-42^{\circ}$ . (Found: N, 9.6.  $C_{16}H_9O_8N_4Cl_5$  requires N, 9.9 per cent).

The same condensation was also carried out though less conveniently using chloro-sulphonic acid (45 g.) when, after four crystallisations, pure product (m. p.  $81^{\circ}$ ) was obtained.

*Dehydrohalogenation of  $\alpha$ -bis-(p-Chlorophenyl)- $\beta\beta\gamma$ -trichloro-n-butane and Oxidation of the crude Dehydrohalogenated Compound.*—Pure compound (2 g.) was dissolved in absolute alcohol (10 c.c.) and to this was added potassium hydroxide (2 g.) dissolved in minimum quantity of water. This was refluxed on a water-bath for half an hour. The alcohol was then removed and the residue was extracted with ether, the extract washed, dried and the ether evaporated. Yellowish paste was isolated which could not be crystallised, and hence was directly subjected to oxidation.

The unsaturated compound obtained as above (1.5 g.) was dissolved in acetone and potassium permanganate (about 30 g.) was added. The whole mixture was then heated on a water-bath for about an hour. Sulphur dioxide was then passed to dissolve the precipitated manganese dioxide. It was then extracted with ether, the extract washed, dried and the ether removed. The product after crystallisation from alcohol was found to be *pp'*-dichlorobenzophenone, m.p.  $142-44^{\circ}$  (Grummitt, Buck and Jenkins, *J. Amer. Chem. Soc.*, 1945, **67**, 155, record m.p.  $143-44^{\circ}$ ). The mixed melting point of this with *pp'*-dichlorobenzophenone obtained from DDT was not depressed.

The 2:4 dinitrophenylhydrazones gave bright red crystals, m.p. and mixed m.p. with an authentic specimen from *pp'*-dichlorobenzophenone,  $230^{\circ}$ . (Found: N, 13.1  $C_{16}H_{13}O_4N_4Cl_2$  requires N, 13.1 per cent).

*Condensation of Butylchloral Hydrate with Bromobenzene:  $\alpha$ -bis-(p-Bromophenyl)- $\beta\beta\gamma$ -trichloro-n-butane.*—Butylchloral hydrate (24 g.) was condensed with bromobenzene (47.1 g., 20% excess) in presence of oleum (5%, 100 g.) at  $45^{\circ}$ , the stirring being continued for 6 hours. The reaction mixture was then poured over ice, when a pasty product was obtained. This was washed as in the previous case and subjected to steam-distillation when the unreacted substances passed over. The product that remained was crystallised from alcohol, m.p.  $97-99^{\circ}$ , yield 20 g. (Found: Cl, 21.6; Br, 36.3.  $C_{18}H_{13}Cl_3Br_2$  requires Cl, 22.5; Br, 33.9 per cent).

The crude dehydrohalogenated product, obtained from the above compound (2 g.) after refluxing it with alcoholic potassium hydroxide (2 g.) was directly oxidised by boiling with chromic acid (2 g.) in acetic acid for 2 hours. It was diluted, neutralised with sodium bicarbonate, extracted with ether and the extract dried. On removal of ether *pp'*-dibromobenzophenone (m.p.  $172^{\circ}$ ) was obtained (Hoffmann, *Annalen*, 1891, **264**, 163, records m.p.  $172-73^{\circ}$ ). Oxime, m.p.  $145-49^{\circ}$  (Hoffmann, *loc cit.*, m.p.  $145-49^{\circ}$ ).

*Condensation of Butylchloral Hydrate with Benzene:  $\alpha$ -bis-(Phenyl)- $\beta\beta\gamma$ -trichloro-n-butane.*—Butylchloral hydrate (24 g.) was condensed with benzene (25 g.) in presence of oleum (4%, 200 g.) at  $29-31^{\circ}$  for 6 hours. This was then poured over ice when the solid product was obtained. This was washed well with water and crys-

tallised from alcohol when white needles (yield 18 g.), m.p. 83-84°, were obtained. (Found : Cl, 33.9.  $C_{18}H_{15}Cl$ , requires Cl, 33.9 per cent).

The crude product obtained on dehydrohalogenation of the above compound (2 g.) with alcoholic potassium hydroxide was oxidised by refluxing with chromic acid (4 g.) in acetic acid for 4 hours. On working up a yellowish liquid was isolated. This may be the labile form of benzophenone, m.p. 26-26.5° (Zincke, *Annalen*, 1871, 159, 378, 381).

2 : 4-Dinitrophenylhydrazones, m.p. and mixed m.p. with an authentic specimen from benzophenone, 233-34° (Found : N, 15.2.  $C_{19}H_{15}O_4N_4$  requires N, 15.4 per cent).

*Condensation of Butylchloral Hydrate with Naphthalene* :  $\alpha$ -bis-( $\alpha$ -Naphthyl)- $\beta\beta\gamma$ -trichloro-*n*-butane.—The solid product obtained from butylchloral hydrate (24 g.), naphthalene (35.2 g.) and oleum (4%, 100 g.) at 45° for 3 hours, was washed well and crystallised from *n*-propyl alcohol. After several crystallisations, pure product of m.p. 196-98° was obtained (poor yield). (Found : Cl, 26.1.  $C_{24}H_{19}Cl_3$  requires Cl, 25.7 per cent).

Attempt to dehydrohalogenate the pure compound (1 g.) by refluxing it with alcoholic potash (1 g.) for 4 hours was unsuccessful, the original compound being recovered unchanged. Direct oxidation with chromic acid in acetic was attempted but no definite product could be isolated.

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# PRODUCTION OF THE JOSHI EFFECT IN OXYGEN UNDER SILENT ELECTRIC DISCHARGE. PART VI INFLUENCE OF THE EXCITING POTENTIAL, THE GAS PRESSURE AND THE MATERIAL OF THE CENTRAL H.T., UNDER SEMI-OZONISER EXCITATION

BY S. R. MOHANTY

The Joshi effect  $\Delta i$  has been studied in oxygen in the range 10-500 mm Hg ( $p$ ) and excited over 0.5 to 4 kilo-volts (V) of 50 cycles frequency in semi-ozonisers with Pt, Au, Ag and Cu central H.T. electrodes. The 'threshold potential'  $V_m$  is sensibly a linear function of  $p$ .  $\Delta i$  sets in near  $V_m$ . Above  $V_m$ , the net effect  $\Delta i$  at constant  $p$  first increases with  $V$  and then decreases. The relative effect %  $\Delta i$  is a maximum near  $V_m$ , and diminishes thereafter.  $\Delta i$  increases with  $p$  up to a limiting pressure and then decreases. These results are similar to those observed for the gas in Siemens' tubes.  $\Delta i$  is influenced by the nature of the central H.T. This is traced to the differences in the photo-electric activity of the chemically adsorbed layers of oxygen.

It was observed by Joshi (*Proc. Indian Sci. Cong.*, 1943, Part II, pp. 70-75) that the above effect  $\Delta i$  occurs to more than a detectible extent in chlorine subjected to ionisation by collision in wire-in-cylinder type discharge tubes or semi-ozonisers. Apart from this, all previous work on this phenomenon referred chiefly to the Siemens' tube as the excited system. The present work, which is an extension of the preliminary investigations of the author (Mohanty, *ibid.*, 1948, Part III, *Chem. Sec.*, Abst. No. 36), refers to variation with the applied potential  $V$ , the gas pressure  $p$ , and the material of the central H.T. electrode of the Joshi effect in oxygen under semi-ozoniser excitation.

## EXPERIMENTAL

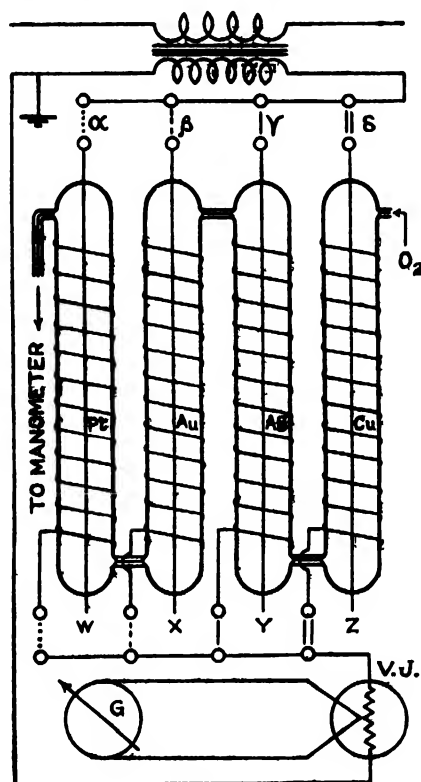
The general assemblage of apparatus and the experimental procedure were essentially similar to those described in Part I (Mohanty and Kamath, this *Journal*, 1948, 26, 405). Four semi-ozonisers (Fig. 1) of equal dimensions\* and designated W, X, Y and Z were used; the central H.T. electrodes were respectively of platinum, gold, silver and copper. The low tension electrode in each case was represented by a helix of bright copper wire (the distance between consecutive turns being sufficiently large to permit irradiation of the enclosed gas) on the outer (glass) tube. The discharge current  $i$  was observed with a sensitive mirror galvanometer G actuated by a Cambridge vacuo-junction V.J. (Fig. 1). The source of light was a 200 watt incandescent (glass) bulb run at 200 volts, and placed at a distance of 25 cm. from the discharge tubes.

Oxygen, prepared and purified as described in Part I (Mohanty and Kamath, *loc. cit.*), was introduced into the semi-ozonisers at various  $p$  in the range of 10 to 450 mm.

Outer diameter of the glass cylinder	5 mm.
Inner " "	4
Thickness of the glass wall	0.5
Diameter of the central H.T. electrode	0.25
Length of the electrode space	13.5 cm.

Hg in the case of W, and 150 to 450 mm. in the case of the other three semi-ozonisers. The gas was subjected to different alternating  $V$  varied over 0.5 to 4 kV (r.m.s.) of 50

FIG. 1  
*Joshi effect in  $O_2$  under semi-ozoniser excitation.*



cycles frequency. Galvanometer deflections were noted in dark and under irradiation; from these, the discharge current in dark  $i_d$ , that under irradiation  $i_l$ , the net effect  $\Delta i$  and the relative effect  $\% \Delta i$  were calculated. The results are shown in Table I.

## DISCUSSION

It was shown earlier (Mohanty and Kamath, *loc. cit.*) that *ceteris paribus*  $V_m$  (defined as the minimum 'threshold potential' at which  $i$  increases rapidly with the applied  $V$ , and obtained by extrapolation of the  $V-i_b$  characteristics) for oxygen subjected to alternating fields in Siemens' tubes was sensibly a linear function of  $p$  over a fairly wide range. That the pressure variation of  $V_m$  for the gas excited in semi-ozonisers is similar, except at comparatively low pressures, is evident from Fig. 2.  $V_m$  increases linearly from 0.69 kV at 100 mm. to 1.69 kV at 450 mm. Below 100 mm.,  $V_m$  falls off more rapidly than  $p$ ; this might result from inaccuracy in fixing  $V_m$  for these pressures, since the  $V-i$  characteristics are more horizontal.

The influence of the exciting  $V$  on  $\Delta i$  and  $\% \Delta i$  in oxygen under semi-ozoniser excitation is similar to that observed for the gas in Siemens' tubes (Mohanty and Kamath, *loc. cit.*).



TABLE I (contd.)

Central H.T.	V (kilo-volts r.m.s.)	Platinum								Gold				Silver				Copper			
		10	50	100	150	200	250	350	450	150	250	350	450	150	250	350	450	150	250	350	450
1.47	$i_p$		7.42	10.40	9.9	7.28	4.58			6.16	4.69			6.16	3.00			4.9	4.24		
	$i_c$		6.78	8.83	7.68	5.48	3.74			5.1	3.87			5.83	2.35			4.58	3.87		
	$\Delta i$		0.64	1.57	2.22	1.80	0.84			1.06	0.82			0.33	0.65			0.32	0.37		
	% $\Delta i$		8.6	15.1	22.4	24.7	18.3			17.2	17.5			5.4	21.7			6.5	9.7		
1.6	$i_p$	3.87	7.75	11.09	10.95	8.31	6.48	1.73													
	$i_c$	3.46	7.07	9.54	8.54	6.16	4.9	1.00													
	$\Delta i$	0.41	0.68	1.55	2.41	2.15	1.58	0.73													
	% $\Delta i$	10.6	8.8	14	22.0	25.9	24.4	42.2													
1.73	$i_p$		8.06	11.79	11.92	9.22	7.28	4.36		7.25	5.92	3.87		7.78	4.24	3.16		5.48	4.64	3.46	
	$i_c$		7.42	10.35	9.38	7.00	5.57	3.32		6.36	5.00	3.16		7.35	3.39	2.65		5.29	4.30	3.16	
	$\Delta i$		0.64	1.44	2.54	2.22	1.71	1.04		0.89	0.92	0.71		0.43	0.85	0.51		0.19	0.34	0.30	
	% $\Delta i$		7.9	12.2	21.3	24.1	23.5	23.9		12.3	15.5	18.4		5.5	20.0	16.1		3.5	7.3	8.7	
1.87	$i_p$	4.12	8.31	12.46	12.76	10.10	8.00	6.08	5.1												
	$i_c$	3.74	7.68	11.00	10.10	7.68	6.25	4.69	4.00												
	$\Delta i$	0.38	0.63	1.46	2.66	2.42	1.75	1.39	1.1												
	% $\Delta i$	9.2	7.6	11.7	20.8	24	21.9	22.9	21.6												
2	$i_p$		8.60	13.04	13.23	11.00	8.94	7.42	6.86	8.25	6.63	4.8	2.74	8.83	5.39	4.58	3.24	6.08	4.9	4.12	3.08
	$i_c$		8.00	11.68	10.58	8.57	7.07	5.75	5.39	7.42	5.61	3.87	2.45	8.31	4.53	3.74	2.83	5.92	4.69	3.74	2.83
	$\Delta i$		0.60	1.46	2.65	2.63	1.87	1.67	1.47	0.83	1.02	0.93	0.29	0.52	0.86	0.84	0.41	0.16	0.21	0.38	0.25
	% $\Delta i$		7	11.2	20.0	23.9	20.9	22.5	21.4	10.1	15.4	19.4	10.6	5.9	16	18.3	12.7	2.6	4.3	9.2	8.1
2.13	$i_p$	4.53	8.83	13.68	14.18	11.88	9.85	8.43	8.72												
	$i_c$	4.12	8.19	12.21	11.53	9.17	7.75	6.48	6.93												
	$\Delta i$	0.41	0.64	1.47	2.65	2.71	2.10	1.95	1.79												
	% $\Delta i$	9.1	7.2	10.8	18.7	22.8	21.3	23.1	20.5												
2.27	$i_p$		9.06	14.25	14.73	12.73	10.63	9.38	9.85	9.33	7.55	5.79	5.29	10.1	6.40	5.66	5.57	6.71	5.2	4.36	3.87
	$i_c$		8.43	12.80	12.28	10.00	8.43	7.28	7.81	8.60	6.40	4.8	4.24	9.54	5.57	4.69	4.36	6.56	5.00	4.00	3.54
	$\Delta i$		0.63	1.45	2.45	2.73	2.20	2.10	2.04	0.73	1.15	0.99	1.05	0.56	0.83	0.97	1.21	0.15	0.2	0.36	0.33
	% $\Delta i$		7	10.2	16.6	21.05	20.7	22.4	20.7	7.8	15.2	17.1	19.9	5.5	13	17.1	21.7	2.2	3.8	8.3	10.7



TABLE I (contd.)

[illegible]

FIG. 2

Variation with gas pressure  $p$  of the threshold potential,  $V_m$  for oxygen.

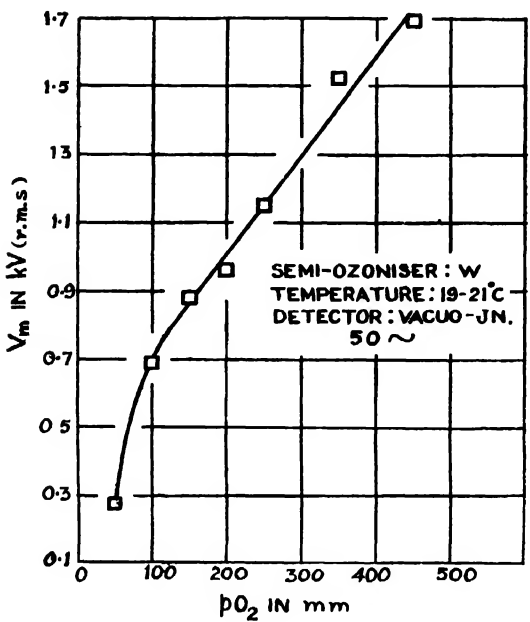
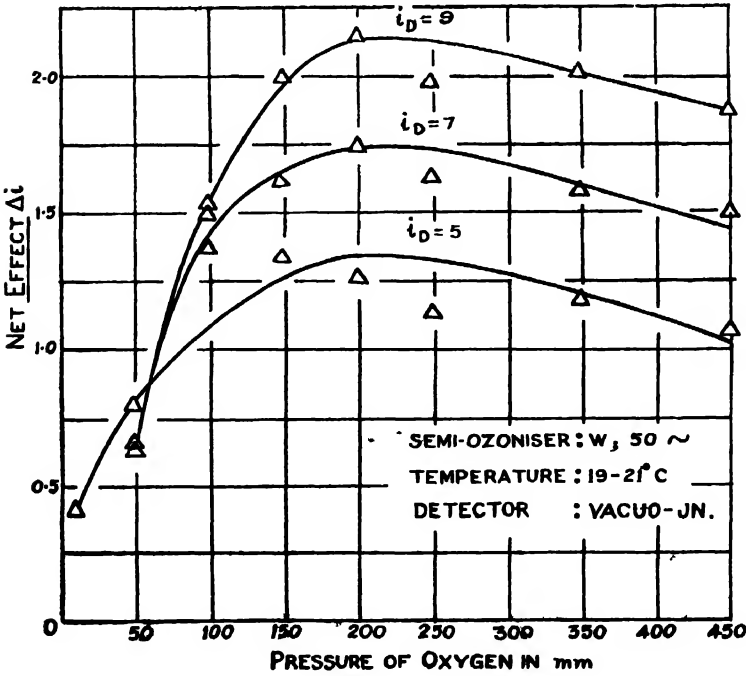


FIG. 3

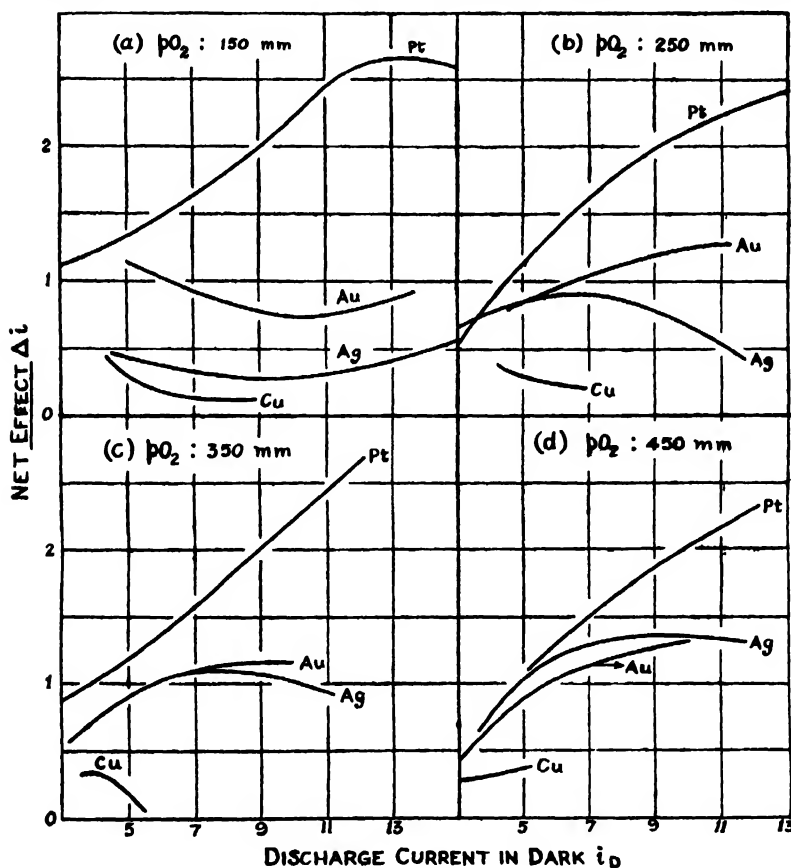
Pressure variation of the Joshi effect in oxygen at const.  $i_D$ .



$\Delta i$  sets in only near  $V_m$ . With  $V$  increased progressively beyond  $V_m$ , the net effect  $\Delta i$  increases to a maximum and then decreases (Table I). Thus e.g.,  $V_m$  at 150 mm. is 0.88 kV. At this pressure  $\Delta i$  sets in (1.00) at 0.93 kV, increases to a maximum of 2.65 at 2 kV, and falls off to 2.45 with further increase of  $V$  to 2.67 kV. Similar to results with Siemens' tubes (Mohanty and Kamath, *loc cit.*), the applied  $V$  corresponding to maximum  $\Delta i$  increases with  $p$ . Thus,  $V$  for maximum  $\Delta i$  at 100 mm. is 1.33 kV; that at 150 mm. is 2 kV. Further, the increase of  $\Delta i$  is distributed over a wider range of  $V$  at higher than at low  $p$ . Thus e.g., whilst at  $pO_2 = 100$  mm.,  $\Delta i$  increases over a range of 0.53 kV, it does so over 1.07 kV at 150 mm. The proportionate effect  $\% \Delta i$  is maximum near  $V_m$  and diminishes with  $V$ . Thus, at 150 mm. ( $V_m = 0.88$  kV),  $\% \Delta i$  sets in and is maximum (50.0) at 0.93 kV and diminishes to 14.8 at 2.67 kV.

FIG. 4

Influence of central H. T. on Joshi effect in  $O_2$  under semi-ozonisers.



It is seen from Fig. 3 that  $\Delta i$  at constant  $i_D$  increases with  $p$ , at first rapidly and then slowly, to a maximum at  $pO_2 = 200$  mm., followed by a slow decrease afterwards. Thus, for  $i_D = 7$ ,  $\Delta i$  at 50 mm. is 0.67. It increases to 1.5 at 100 mm., to 1.75 at 200 mm., and is reduced to 1.50 at 450 mm. The influence of  $p$  on  $\Delta i$  in oxygen (Mohanty and Kamath, *loc. cit.*), chlorine (Deo, *Proc. Indian Sci. Cong.*, 1945, Part III, *Phys.*

Sec., Abst. No. 13; Joshi and Deo, *Nature*, 1944, **153**, 434) and bromine (Rao, unpublished results) subjected to alternating fields in Siemens' tubes is similar.

The present experiments reveal that the magnitude of  $\Delta i$  in oxygen under semi-ozoniser excitation is markedly altered by a change in the material of the central H.T. electrode. At  $pO_2=150$  mm. (Fig. 4), e.g.,  $\Delta i$  at a given  $i_0$  varies in the order:  $Pt > Au > Ag > Cu$ ; the effect with the last electrode is very small. At higher  $p$ , viz., 350 and 450 mm.,  $\Delta i$  values with Au and Ag electrodes coincide within the limits of experimental error. This influence of the material of the central H.T. electrode on  $\Delta i$  is independent of the mode of current detection. Thus, the author and Pradhan (*Proc. Indian Sci. Cong.*, 1948, Part III, *Phys. Sec.*, Abst. No. 19) working with gold, silver and copper electrodes found that the effect observed with a diode used as half-wave detector varied in the same order.

According to Joshi (*ibid.*, 1946, Part III, *Phys. Sec.*, Abst. No. 26; 1947, Part III, *Phys. Sec.*, Abst. No. 25; *Curr. Sci.*, 1946, **15**, 281; 1947, **16**, 19), photo-electron emission from an adsorption-like ionic + molecular boundary layer formed on the electrodes under discharge, is primary to  $\Delta i$ . Oxygen is adsorbed chemically on Pt, Au, Ag and Cu (McBain, "The Sorption of Gases and Vapours by Solids", George Routledge, 1932, Chapter IX). Emission of photo-electrons from these metals is not possible under the light-band used, since the short-wave limit, viz.,  $3700\text{\AA}$  (Mohanty and Kamath, this *Journal*, 1948, **25**, 467) is higher than the threshold wavelengths of the metals, outgassed or not (Hughes and DuBridge, "Photoelectric Phenomena", McGraw-Hill, 1932, pp. 75, 76). Since the work-function, as also the spectral sensitivity of the boundary layers, will be different, variation in  $\Delta i$  is to be anticipated. The smoothness of the metallic surface is another consideration. A rough surface possesses a large area exposed to the gas; adsorption, and hence,  $\Delta i$  will be large.

Grateful thanks of the author are due to Professor S. S. Joshi for suggesting the problem, and for his kind interest and valuable guidance.

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## PHYSICAL STRUCTURE OF METALS IN RELATION TO THEIR CATALYTIC BEHAVIOUR. PART I. LANGMUIR SURFACES

By B. S. SRIKANTAN

Metals with face-centred cube lattice structure and high vibrational energy at their melting points are good catalysts.

Langmuir (*J. Amer. Chem. Soc.*, 1916, 38, 2221) extended Bragg's work on crystals to chemical reactions taking place in heterogeneous systems. Surface atoms in a solid possessing residual affinities constitute a "checker board" where gases or adsorbed molecules may anchor on till chemical action or desorption takes place. He considered metal surfaces like platinum and tungsten and showed theoretically and experimentally that simple reactions like the dissociation of hydrogen molecules into atoms could be well accounted for. He has further shown that the atoms in a metal catalyst though vibrating about a centre are held rigidly (*Phys. Rev.*, 1916, 8, 149) and there is no gradation of layers of atoms varying in density from the solid to the gas surrounding, but the change from the solid to the gas is abrupt and adsorption is mono-molecular in thickness. His experiments conclusively proved his theory.

Taylor (*Proc. Roy. Soc.*, 1925, 108A, 105) put forward a theory of active centres on the evidence of (i) lack of correlation between catalytic activity and adsorption, (ii) the extraordinary heat sensitivity of the catalyst material (Smith *et al.*, *J. Chem. Soc.*, 1921, 121, 1613; 1923, 123, 2088), (iii) the poisoning of catalysts in stages (Vavon and Husson, *Compt. rend.*, 1922, 175, 277), and (iv) very great variations in the energy of adsorption of gases for different parts of the surface (Garner and Blench, *J. Chem. Soc.*, 1924, 1288). Reserving a detailed examination of these points to later communications, it has to be observed, that most of the work on catalysis deals with complex reacting substances and also different types of solid substances as catalyst materials. Mono-atomic metals, semi-conductors, ionic valence type crystals and amorphous substances have all been used. It is not surprising therefore that the simple idea of Langmuir had to be modified. In this paper, assuming the Langmuir surface is basically correct, an attempt has been made to review the physical properties of metallic types of solids in relation to their catalytic behaviour. The physical properties of different types of solids are different from each other, and arise from their structure. In the conclusions arrived at here, a certain amount of empirical factor is unavoidable but their usefulness must be conceded only from the large number of cases they reasonably cover.

### *Types of Structures*

Most of the metals belong to one of the three types: B.C.C., F.C.C. and C.P.H. The adsorption of reacting molecules takes place through the valence forces of the surface atoms.

In Table I are summarised some of the physical characteristics of metals belonging to different groups. It is noticeable that most of the metals usually used in different reactions as catalysts are F.C.C. types and then a few C.P.H. types. In the conversion of benzene in to cyclohexane by metal catalysts, Long, Frzer and Ott (*J. Amer. Chem. Soc.*, 1934, 56, 1101) found that B.C.C. structures were inactive while the F.C.C. ones were active.

TABLE I

Metals.	Type of lattice.	M. p.	$m\mu^2 \times 10^{-22}$	$t_r \times 10^{-18}$	$t_r/6\lambda$
<b>Group I</b>					
Copper	F.C.C.	1356°K	105	4.2	$4.7 \times 10^{-4}$
Silver	F.C.C.	1234	104*	3.5	$2.5 \times 10^{-4}$
Gold	F.C.C.	1336	107	4.8	$2.7 \times 10^{-4}$
<b>Group II</b>					
Magnesium	C.P.H.	932	73		...
Calcium- $\alpha$	F.C.C.	1123	83	..	.
Calcium- $\beta$	C.P.H.	"	"	.	.
Strontium	F.C.C.	1044	85	..	
<b>Group III</b>					
Aluminium	F.C.C.	933	73		$8.3 \times 10^{-4}$
Lanthanum- $\alpha$	C.P.H.	1085	95*	6.6	...
Lanthanum- $\beta$	F.C.C.	"	"	"	
Thallium- $\alpha$	C.P.H.	576	32*		...
Thallium- $\beta$	F.C.C.	"	"		...
<b>Group IV</b>					
Titanium	C.P.H.	2073	165	...	...
Tin- $\alpha$ (grey)	T.C.	505	39	22.2	$8.2 \times 10^{-4}$
Tin- $\beta$ (white)	B.C.T.	"	"	"	"
Thorium	F.C.C.	1953 to 2053	169	...	...
Lead	F.C.C.	600	48	33.6	$1 \times 10^{-4}$
<b>Transition group</b>					
Vanadium	B.C.C.	1993	156	...	...
Chromium- $\alpha$	B.C.C.	2103	137	23.9	$3.3 \times 10^{-3}$
Chromium- $\beta$	C.P.H.	"	"	"	"
Manganese- $\alpha$	Cubic	1515	117	..	...
Manganese- $\beta$	Complex	"	"	..	..
Manganese- $\gamma$	Tet, F.C.	"	"	..	..
$\alpha\beta\gamma$ -Iron	B.C.C.	1808	142	20.68	$2.9 \times 10^{-3}$
$\gamma$ -Iron	F.C.C.	"	"	"	"
Cobalt- $\alpha$	C.P.H.	1763	140	23.73	$3.2 \times 10^{-3}$
Cobalt- $\beta$	F.C.C.	"	"	"	"
Nickel- $\alpha$	C.P.H.	1725	146	27.97	$3.8 \times 10^{-3}$
Nickel- $\beta$	F.C.C.	"	"	"	"
Rhodium	F.C.C.	2239	...	...	...

TABLE I (contd.)

Metals.	Type of lattice.	M. p.	$mr^2\nu^2 \times 10^{-22}$	$t_r \times 10^{-10}$	$t_r/6\lambda$
Palladium	F.C.C.	1827	133	22.39	$2.2 \times 10^{-3}$
Tungsten- $\alpha$	B.C.C.	3643	...	7.52	...
Tungsten- $\beta$	F.C.C.	"	...	"	...
Osmium	C.P.H.	2973 ?	207	...	...
Iridium	F.C.C.	2827	195	25.69	$2.1 \times 10^{-3}$
Platinum	F.C.C.	2046	162	18.78	$1.4 \times 10^{-3}$
<i>Non-metal</i>					
Graphite			278	120.6	$6.0 \times 10^{-1}$

Note :—(1) The m.p. s. are taken from Kaye and Laby ("Physical and Chemical Constants", 1944).

(2)  $mr^2\nu^2 \times 10^{-22}$  from Srikantan (*Indian J. Phys.*, 1930 **4**, 540).

(3)  $tr = 3k/hd$  where  $K$  is the Boltzman's constant and  $h$ , heat conductivity of solids (*Metals Hand-book*, 1939) and  $d$  is distance between the atoms (Seitz, "Modern Theory of Solids", 1940).

(4)  $\lambda$  the reciprocal of atomic frequency  $\nu$  (Lewis, "Physical Chemistry", 1921, III, p. 61).

(5) The peculiarity of iron is discussed under allotropic changes.

\* These values have been recalculated.

### Energy of Vibration of Atoms

In Table I, there are a few exceptions to the conclusions drawn above. Calcium ( $\alpha$ ), strontium, aluminium, thallium and lead are not preferred as catalysts, though they are F.C.C. in type. They may enter into chemical reactions and may even act as catalytic poisons. Lead, for example, is not a catalyst but is known to poison active materials. It appears therefore that the availability of greater number of atoms in the surface or lattice planes is not the only factor of importance, but these atoms must be capable of activating the adsorbed molecules. The author has shown (*Indian J. Phys.*, 1930, **4**, 539) that the energy of vibration ( $4\pi mr^2\nu^2$ ) of an atom is a matter of decided importance in catalysis. (The terms are explained in the paper cited). It is to be noted that F.C.C. or C.P.H. lattice metals, which have a value for this ( $mr^2\nu^2$ ) energy term below  $100 \times 10^{-22}$  exhibit low catalytic activity. Thus aluminium, thallium( $\beta$ ) and lead, though F.C.C. in type, have low values for energy of vibration of atoms and are not catalytic. There are also other metals having a high value but not F.C.C. types. They are not also catalysts. Therefore the above conclusion could be modified that all metals having F.C.C. structures and vibrational energy of their atoms more than  $4\pi 100 \times 10^{-22}$  are good catalysts.

In the last column in Table I ( $t_r/6$ ),  $t_r$  gives the time necessary for the temperature increment of the surface layer of one of the faces of a cube of a metal to fall to 37% of its initial value (Langmuir, *loc. cit.*) and  $\lambda$  is the time of oscillation of an atom, for the various metals. The metals of the non-transitional group are 1000 times more rigid than graphite, while those of the transitional group are only 100 times so. It is not surprising therefore that catalysts are to be chosen more often from the transitional group than from other groups.

*Allotropic Changes*

Metals of the transition group exhibit the phenomena of allotropism at ordinary pressures. The most important are iron, cobalt and nickel. A change in physical characteristics, and hence a change in catalytic properties, is to be expected from these allotropic modifications of the metals.  $\alpha$ -Tungsten is of B.C.C. type and  $\beta$ -tungsten is of valence type of crystal and its activity is similar to that of graphite. In fact that adsorption on tungsten surfaces is akin to chemical compound formation (Chemisorption) is evident from the work of Langmuir (*loc. cit.*). The nature of the lattice planes in  $\alpha$ -iron is exceptional though  $\alpha$ -iron is of B.C.C. type it would show some catalytic properties. The B.C.C. form is stable between  $0^\circ$  and  $1179^\circ\text{K}$  and between  $1674^\circ$  and  $1808^\circ\text{K}$ , while  $\gamma$ -form is stable between  $1179^\circ$  and  $1679^\circ\text{K}$ . Most of the prepared iron catalysts are in the B.C.C. region. However, Hisen-lut and Kaupp (*Z. physikal Chem.*, 1928, 133, 459; *Z. Elektrochem.*, 1930, 36, 392) find that on adsorption of nitrogen the B.C.C. type changes to F.C.C. in the case of iron. The work of Fischbeck (*Z. Elektrochem.*, 1934, 40, 517) on the decomposition of ammonia by iron shows increased activity as the iron changes to  $\gamma$ -form *i.e.*, F.C.C. type.

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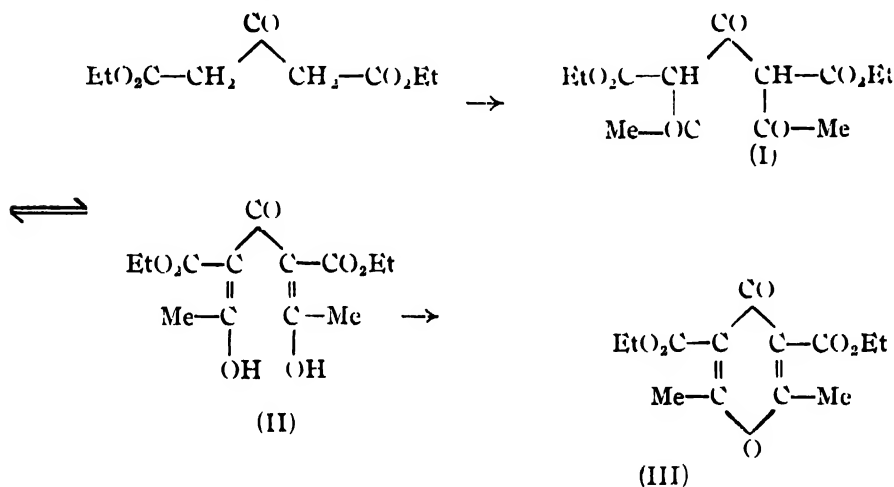


## DIFORMYLACETONE DICARBOXYLIC ESTER AND DIFORMYLACETONE

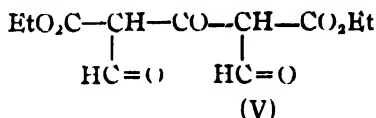
BY M. M. MHALA AND S. S. DESHPANDE

The syntheses of 1:3:5-triketones, namely  $\alpha\alpha'$ -diformylacetone dicarboxylic ester and  $\alpha\alpha'$ -diformylacetone have been described

By the action of acetyl chloride on the disodium derivative of acetone dicarboxylic ester Peratoner and Strazzeri (*Gazzetta*, 1891, 21, 1, 298) obtained 2:6-dimethylpyrone dicarboxylic acid 3:5-diethyl ester (III). The dienol form (II) of the diacetyl derivative (I), which must have been first formed, lost one molecule of water under the conditions of the experiment closing thereby the pyrone ring



In an attempt to synthesise 1:3:5-triketones  $\text{—CO—CH—CO—CH—CO—}$  (IV), two of which are described in the present paper, we aimed at producing  $\alpha\alpha'$ -diformyl derivatives of ketones. By treating formic ester with acetone dicarboxylic ester in presence of two atoms of sodium at the temperature of ice we obtained a disodium derivative which, when acidified in cold, yielded  $\alpha\alpha'$ -diformylacetone dicarboxylic ester,  $\text{C}_{11}\text{H}_{14}\text{O}_7$  (V)



That the compound is not a pyrone follows from the result of its analysis and from the following facts:— (i) It has none of the properties of a pyrone. (ii) It forms a semicarbazone (pyrones do not). (iii) It gives violet coloration with ferric chloride. (iv) It forms a non-chelate copper salt  $\text{C}_{11}\text{H}_{12}\text{O}_7\text{Cu}$  as 1:3:5-triketones do, from which on acidification the original ketone is regenerated.

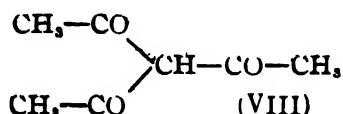
Certain syntheses with acetone, in which two reactive methyl groups— one on each side of the carbonyl— are theoretically available for condensation, are, however, better

effected by using acetone dicarboxylic acid or its ester. For instance, by the action of nitrous acid on acetone dicarboxylic acid Pechmann and Wehsang (*Ber.*, 1886, 19, 2465) obtained  $\alpha\alpha'$ -diisonitrosoacetone,  $\text{HON}=\text{CH}-\text{CO}-\text{CH}=\text{NOH}$  (VI).

In the molecule of acetone, when one of the two methyl groups has reacted, further reaction generally does not take place at the second methyl group to produce an  $\alpha\alpha'$ -product, but again at the first to produce  $\alpha\alpha'$  product. Thus, when acetylacetone (VII) in the formation of which one of the two methyl groups of acetone has reacted, is further acetylated, the product formed is  $\alpha\alpha'$ -diacetylacetone (VIII) (Nef, *Annalen*, 1893, 277, 71).



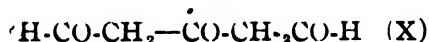
(VII)



(VIII)

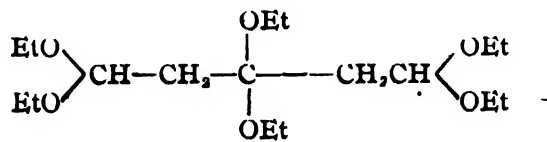
When, however, sodium derivative of acetone monoxalic ester reacts with sodium ethylate and oxalic ester (Claisen, *Ber.*, 1891, 24, 116), or when oxalic ester (2 mols.) acts upon acetone (1 mol.) and sodium ethylate (2 mols.) in two instalments (Willstätter and Pummerer, *Ber.*, 1904, 37, 3734) the product formed is the disodium derivative of  $\alpha\alpha'$ -acetone-dioxalic ester,  $\text{EtO}_2\text{C}-\text{CO}-\text{CH}_2-\text{CO}-\text{CH}_2-\text{CO}-\text{CO}_2\text{Et}$  (IX)

With a view to studying the action of two molecules of formic ester on acetone, we added to sodium (1 atom) a mixture of the ester (1 mol.) and acetone (1 mol.) and then another atom of sodium and another mol. of the ester. We also worked by adding to sodium (2 atoms) a mixture of the ester (2 mols.) and acetone (1 mol.). The reaction was carried out at ice temperature and in ether as the solvent. In both the cases we obtained a disodium derivative which on acidification gave  $\alpha\alpha'$ -diformylacetone,  $\text{C}_5\text{H}_6\text{O}_3$  (X)



which is the simplest 1:3:5-triketone.

Diformylacetone (*bis*-hydroxymethylene acetone) was obtained in aqueous solution by Willstätter and Pummerer (*Ber.*, 1905, 38, 1470) by hydrolysing its *tris*-diethylacetal,

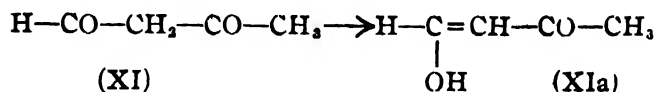


which in its turn was prepared from 1:4-pyrone and *ortho*formic ester. They, however, did not isolate the pure ketone from its aqueous solution and did not analyse it. They also have not described any of its functional derivatives except its green copper salt,  $\text{CuC}_5\text{H}_4\text{O}_3$ .

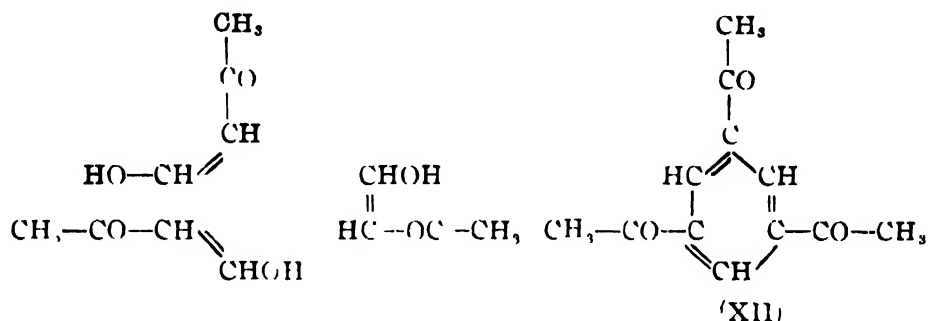
The compound isolated by us is a liquid and very soluble in water. Its composition has been proved from its analysis. It forms a semicarbazone and gives a violet coloration with ferric chloride. Like other 1:3:5-triketones it forms a non-chelate copper salt,  $\text{CuC}_5\text{H}_4\text{O}_3$ , the properties of which agree with those described by Willstätter and Pummerer (*loc. cit.*). On standing for some days it gradually turns into a brown solid

which we have not yet investigated. Simultaneously the intensity of its coloration with ferric chloride fades.

In the reaction described above an appreciable amount of monoformylacetone (XI) was formed, which in the hydroxymethylene form (XIa)



readily turned into its self-condensation product, 1:3:5-triacetylbenzene (XII) (Claisen and Styrol, *Ber.*, 1888, 21, 1145).



The latter being a solid could be separated from the liquid diformylacetone or its aqueous solution.

In an attempt to obtain diformylcyclohexanone the only product that was isolated proved to be the monoformyl derivative, hydroxymethylenecyclohexanone.

## EXPERIMENTAL

*Diformylacetone Dicarboxylic Ester.*—To pulverised sodium (4.6 g., 2 atoms) covered by dry ether and kept at ice temperature, was gradually added a mixture of ethyl formate (14.8 g., 2 mols.) and acetone dicarboxylic ester (20 g., 1 mol.). The reaction mixture was kept at 0° for 1 day and then at room temperature for 2 days. The disodium derivative formed was filtered at the pump and washed with ether, yield 26 g. It was dissolved in minimum quantity of cold water and the alkaline solution was extracted with ether, made slightly acid with acetic acid and again extracted with ether. The ethereal extract was washed and dried and the solvent removed. The residual liquid (10 g.) was fractionated and the crude diformyl derivative (b. p. 150°-175°) on further fractionation distilled at 174°-176°, yield 3.4 g. (Found: C, 50.9; H, 5.4;  $\text{C}_{11}\text{H}_{14}\text{O}_7$  requires C, 51.1; H, 5.4 per cent)

The compound readily forms a semicarbazone which on crystallisation from hot dilute alcohol melts at 192-93°. (Found: C, 39.7; H, 5.5; N, 30.0.  $\text{C}_{11}\text{H}_{13}\text{O}_7\text{N}$  requires C, 39.1; H, 5.3; N, 29.3 per cent).

It gives a violet colour with ferric chloride and turns blue litmus red. It is appreciably soluble in water. It forms, in almost theoretical amount, a green copper salt on shaking with aqueous solution of copper acetate. The purified copper salt after drying in an oven at 100° was analysed. (Found: Cu, 20.0.  $\text{C}_{11}\text{H}_{12}\text{O}_7\text{Cu}$  requires Cu, 19.8 per cent).

On decomposition with cold dilute hydrochloric acid the copper salt regenerated the diformyl derivative.

*αα'-Diformylacetone.*—To pulverised sodium (6 g., 2 atoms), covered by dry ether and kept at ice temperature, was gradually added during the course of 45 minutes a mixture of acetone (7.5 g., 1 mol.) and ethyl formate (18.5 g., 2 mols.). The reaction initially was vigorous and care was taken not to allow the temperature to go above 0°. The mixture was kept at this temperature for one day with occasional shaking and then was allowed to remain at room temperature for 2 days with shaking as before. The disodium derivative formed was filtered at the pump and washed with ether. The dry salt weighed 27.5 g.

The derivative was dissolved in minimum quantity of ice-cold water and extracted with ether. The aqueous alkaline solution was made slightly acid with acetic acid and left to stand for sometime. Crystals of 1:3:5-triacetylbenzene, produced by self-condensation of monoformylacetone formed in the reaction, began to separate. These were identified from their melting point and the melting point of the semicarbazone. After 2 hours the liquid was filtered from the crystals and extracted five times with chloroform. After washing, drying and removal of the solvent the crude diformylacetone weighed 9 g. On repeated fractionation further amount of the solvent was removed and a liquid boiling between 98° and 101° (3 g.) was collected. (Found: C, 52.5; H, 5.6.  $C_8H_6O_3$  requires C, 52.6; H, 5.26 per cent).

It is a thin colorless liquid, very soluble in water and gives acid reaction. It colours ferric chloride violet. It forms a semicarbazone which on crystallisation from hot dilute alcohol melts at 160°. (Found: C, 33.9; H, 4.9; N, 43.8.  $C_8H_{11}O_3N_2$  requires C, 33.6; H, 5.2; N, 44.2 per cent).

On adding it to a cold concentrated solution of copper acetate the solution became green but no copper salt separated. After standing for some hours a green crystalline copper salt slowly deposited. The salt is appreciably soluble in water. It was washed with minimum amount of cold water and after drying at 100° it was analysed. (Found: Cu, 36.1.  $C_8H_4O_3Cu$  requires Cu, 36.3 per cent). The salt gives a nearly colorless solution in glacial acetic acid. When an aqueous solution of the disodium salt, made just acid with acetic acid, is poured into excess of cold concentrated solution of copper acetate, the copper salt of *αα'*-diformylacetone is obtained as a green crystalline precipitate on rubbing. 28 g. of the sodium salt gave copper salt which on drying weighed 12 g. This on crystallisation from hot water was found on analysis to be identical with the copper salt prepared directly from the ketone.

In this preparation much of the diformylacetone remained dissolved in the aqueous medium and could not be completely extracted by the solvent. It was isolated in the form of copper salt which proved on analysis to be identical with the copper salt described above. Its semicarbazone could also be prepared from the aqueous solution.

## SYNTHESIS OF 6-HYDROXY-3-ALKYL (ARYL)CHROMONES

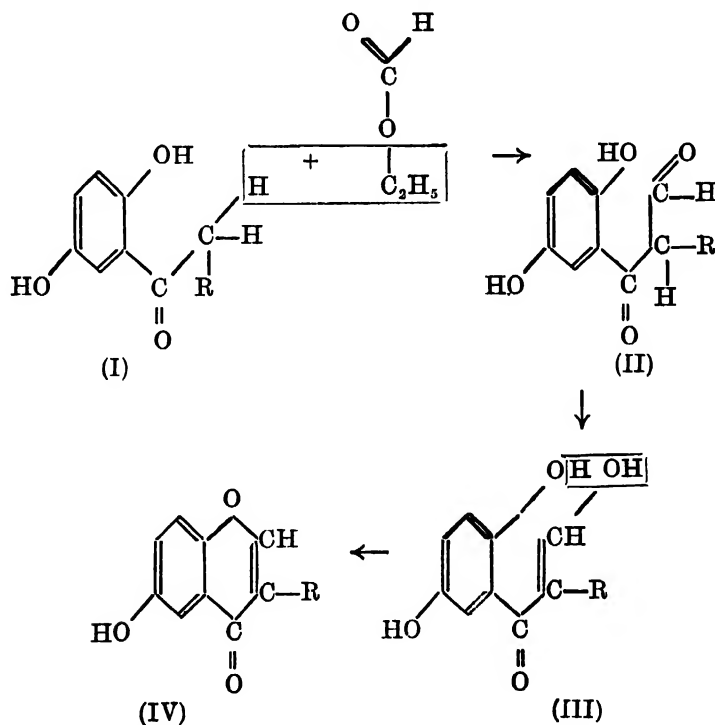
By T.R. INGLE, (LATE) N.L. PHALNIKAR AND B. V. BHIDE

2-Acylhydroquinones on condensation with ethyl formate in the presence of sodium gave 6-hydroxy-3-alkyl(aryl)chromones. The hydroquinones, chromones, as well as their functional derivatives have been described.

A review of the existing literature shows that our knowledge of 6-hydroxycchromones, coumarins and flavones is very scanty, while 6-hydroxy-3-alkyl (aryl) chromones are not at all known. The present paper describes the preparation of such compounds.

Mahal, Rai and Venkataraman (*J. Chem. Soc.*, 1934, 1120) have shown that the *o*-hydroxyphenylbenzyl ketones condense with ethyl formate and give isoflavones, which otherwise were inaccessible or could not be synthesised directly. Using this method acylhydroquinones were condensed with ethyl formate in the presence of sodium to give 6-hydroxy-3-alkylchromones.

Kuroda and Wada (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1938, **34**, 1740) prepared 2-butyrylhydroquinone by Fries' migration of 4-methoxyphenyl butyrate (m.p. 175°). The same ketone has been prepared in this work by (a) the condensation of hydroquinone with butyryl chloride, (b) Fries' migration of hydroquinone dibutyrate, and (c) demethylation of 2-butyrylhydroquinone dimethyl ether.



2-Butyrylhydroquinone, prepared by any one of these methods, however, melted at 101°. Evidently the melting point reported by the above authors appears to be incorrect.

Likewise, Finzi (*Monats*, 1905, 28, 1135) obtained 2-phenylacetylhydroquinone by the condensation of hydroquinone with phenylacetyl chloride and reported the melting point of the substance as  $170^{\circ}$ , while in the present work it melts at  $113^{\circ}$ .

On account of this uncertainty, the acylhydroquinones required in this work were prepared in almost all cases by at least two independent methods and their identity was confirmed by preparing their functional derivatives. The overall yields of the acylhydroquinones, prepared by any of the above methods, were only 5 to 7%.

In order to see the accessibility of the reaction of Mahal, Rai and Venkataraman (*loc. cit.*) this reaction was tried on 2-acetylhydroquinone when 6-hydroxychromone, identical with that obtained by David and Kostanecki (*Ber.*, 1902, 35, 2547) was isolated in good yields. The reactions involved are given above.

By following exactly the same procedure chromones, tabulated in the Table II, have been prepared and their identity confirmed by their functional derivatives.

#### EXPERIMENTAL

*Dimethyl Ether of 2-Butyrylhydroquinone*.—Finely powdered anhydrous aluminium chloride (0.2 M) was added in small lots to a mixture of hydroquinone dimethyl ether (0.2 M), butyryl chloride (0.2 M), dissolved in dry and freshly distilled nitrobenzene (80 c.c.). On keeping overnight, the mixture was heated on a water-bath for 3 hours and then decomposed by ice and hydrochloric acid. The solvent was removed by steam-distillation and the remaining mass was extracted with ether. The ether layer was washed with water, twice with 10% sodium hydroxide solution and again with water. It was then dried over anhydrous magnesium sulphate and the ether removed. The 2-butyrylhydroquinone dimethyl ether, thus obtained, was distilled under reduced pressure, b.p.  $172^{\circ}$ - $175^{\circ}$ /25 mm., yield 70%. (Found: C, 69.2; H 7.8.  $C_{12}H_{16}O_3$  requires C, 69.2; H, 7.7 per cent).

The *semicarbazone*, prepared by the usual method, was crystallised from ethyl alcohol, m.p.  $153$ - $54^{\circ}$ . (Found: N, 15.7.  $C_{13}H_{18}O_3N_2$  requires N, 15.85 per cent).

The *2:4-dinitrophenylhydrazone* was crystallised from methyl alcohol, m.p.  $174$ - $75^{\circ}$ . (Found: N, 14.5.  $C_{18}H_{20}O_6N_4$  requires N, 14.53 per cent).

The other ethers, prepared in a similar manner from hydroquinone dimethyl ether and the requisite acyl chloride, have been described in Table I.

*Preparation of 2-Butyrylhydroquinone. Condensation of Hydroquinone with Butyryl Chloride (Method I)*.—Hydroquinone (0.1 M) and butyryl chloride (0.1 M) were dissolved in dry distilled nitrobenzene (40 c.c.) and freshly powdered anhydrous aluminium chloride (0.1 M) was gradually added to it with ice cooling. On keeping overnight, it was heated on a water-bath for 3 hours, when the colour of the mixture became red. It was then decomposed with ice and hydrochloric acid. The solvent was removed and the residue extracted with ether. The ether extract was dried over anhydrous magnesium sulphate and the ether removed. On keeping overnight it solidified. It was then crystallised from benzene (charcoal), m.p.  $101^{\circ}$ . (Found: C, 66.5; H, 6.7.  $C_{10}H_{12}O_3$  requires C, 66.6; H, 6.66 per cent).

*Dibenzoyl derivative*, prepared by the usual method, crystallised from methyl alcohol in white needles, m.p.  $110^{\circ}$ . (Found: C, 74.25; H, 5.3.  $C_{25}H_{20}O_5$  requires C, 74.2; H, 5.2 per cent).

*Fries Migration of Hydroquinone Dibutyrate (Method II)*.—Hydroquinone dibutyrate was prepared by adding butyryl chloride (0.2 M) to hydroquinone (0.1 M) in small lots with vigorous shaking. When the addition was complete, it was heated on a water-bath for 3 hours and then poured in ice water. The liquid obtained was taken in ether and washed with sodium hydroxide solution (10%) and then with water. The ether extract was dried over magnesium sulphate (anhydrous), and the ether removed. The residue was distilled under reduced pressure. It solidified on cooling. It was crystallised from petroleum ether ( $60^{\circ}$ - $80^{\circ}$ ) in colorless plates, m.p.  $41$ - $42^{\circ}$ . (Found: C, 67.2; H, 7.2.  $C_{14}H_{18}O_4$  requires C, 67.05; H, 7.2 per cent).

Hydroquinone dibutyrate (0.1 M) was thoroughly mixed with finely powdered anhydrous aluminium chloride (0.1 M) and the mixture was heated at  $150^{\circ}$ - $160^{\circ}$  for 5 hours with stirring. On cooling it was decomposed by ice and hydrochloric acid when a black liquid separated. This was taken up in ether, washed first with water and then with 10% sodium hydroxide solution. The alkaline washings were acidified and again extracted with ether. The latter extract on removal of the solvent gave 2-butyrylhydroquinone, which crystallised from benzene (charcoal), m.p.  $101^{\circ}$ .

*Demethylation of Dimethyl Ether of 2-Butyrylhydroquinone (Method III)*.—Dimethyl ether of 2-butyrylhydroquinone (0.04 M) was dissolved in 30 c.c. of hydrobromic acid in acetic acid ( $0^{\circ}$ ). The mixture was heated on a sand-bath for 6 hours under reflux. The whole product was poured on ice when a viscous mass separated. Under these circumstances it was dissolved in ether, and washed with 10% sodium hydroxide solution. The alkaline washings were acidified, extracted with ether, washed free of acids, and dried over anhydrous magnesium sulphate. After removal of the ether, the residue solidified. It was crystallised from benzene, m.p.  $101^{\circ}$ .

All these products obtained by these three different methods have been shown to be identical by finding their mixed melting points.

*Preparation of 6-Hydroxy-3-ethylchromone*.—2-Butyrylhydroquinone (5 g.) was added to dry and freshly distilled ethyl formate (150 c.c.) and the mixture was added to powdered sodium (10 g.) during 2 hours, with ice cooling. After 20 hours the reaction mixture became dull red. It was then decomposed by ice water and it was extracted with ether to remove the unchanged substances. After acidification of the alkaline water extract, and keeping it for about 4 hours, fine needles of 6-hydroxy-3-ethylchromone was obtained. It was filtered and crystallised from dilute ethyl alcohol (charcoal), m.p.  $181^{\circ}$ . (Found: C, 69.2; H, 5.1.  $C_{11}H_{10}O_3$  requires C, 69.3; H, 5.26 per cent).

6-Methoxy-3-ethylchromone was prepared by dissolving the above chromone (1 g.) in dry acetone (20 c.c.) and adding to it anhydrous potassium carbonate (1 g.) and methyl iodide (5 c.c.). The mixture was refluxed for 5 hours. The solid obtained after removal of the solvent was washed with dilute sodium hydroxide and then with

water. It crystallised from petroleum ether (60°-80°), m.p. 66°. (Found: C, 72.4; H, 5.9.  $C_{12}H_{12}O_3$  requires C, 72.24; H, 5.9 per cent).

6-Acetoxy-3-ethylchromone was prepared by refluxing a mixture of 6-hydroxy-3-ethylchromone (1 g.), acetic anhydride (5 c.c.) and anhydrous sodium acetate (1 g.) for 3 hours and pouring it in ice water. The product was crystallised from dilute methyl alcohol, m.p. 90°. (Found: C, 67.4; H, 5.4.  $C_{13}H_{12}O_4$  requires C, 67.3; H, 5.2 per cent).

The other 2-acylhydroquinones, chromones, as well as their functional derivatives have been prepared in a similar manner and are described in Table II.

TABLE I

Compounds. [H=hydroquinone]	Mol formula.	M.p.	B.p.	Found		Calc.		Solvent used and remarks.
				C.	H.	C.	H.	
Dimethyl ether of 2-n-caproyl-H	$C_{14}H_{20}O_3$	—	175-80°/15mm.	71.3%	8.5%	71.2%	8.5%	Colorless liquid.
Dimethyl ether of 2-heptyl-H	$C_{15}H_{22}O_3$	34-35°	175-80°/5	72.1	8.9	72.0	8.8	MeOH
Dimethyl ether of 2-lauroyl-H	—	—	180-85°/1.2	—	—	—	—	B.p. 175-78°/0.2-0.3 mm. (cf. Heilbron <i>et al.</i> , <i>J. Chem. Soc.</i> 1942, 660).
Dimethyl ether of phenylacetyl-H	—	49°	—	—	—	—	—	Petroleum ether (60°-80°), m.p. 49° (cf. Kauffmann and Grombach, <i>Annalen</i> , 1906, 68, 344).
Dimethyl ether of 2-phenylpropionyl-H	$C_{17}H_{18}O_3$	—	210-12°/2-3	75.6	6.8	75.5	6.6	—

TABLE II

Compounds. [C=chromone; H=hydroquinone]	Prepared from.	Mol. formula.	M.p.	B.p.	Found.	Calc.	Solvent used and remarks.
6-Hydroxy-C	2-Acetyl-H & ethyl formate	—	241-42°	—	—	—	M.p. 243° (cf. David and Kostanecki, <i>Ber.</i> , 1902, 35, 2547).
6-Acetoxy-C	6-Hydroxy-C	—	126-27°	—	—	—	M.p. 127° (cf. David and Kostanecki, <i>loc. cit.</i> )
6-Methoxy-C	„	$C_{10}H_8O_3$	97-98°	—	C, 68.3% H, 4.6	68.2% 4.54	Petroleum ether (60°-80°)
2-n-Valeryl-H	H & n-valeryl chloride by method I.	$C_{11}H_{14}O_3$	—	180-85°/15 mm.	C, 68.15 H, 7.2	68.05 7.2	—
6-Hydroxy-3-n-propyl-C	n-Valeryl-H & ethyl formate	$C_{12}H_{14}O_3$	119°	—	C, 70.5 H, 5.8	70.6 5.9	Dilute MeOH



TABLE II (contd.)

Compounds.	Prepared from.	Mol. formula.	M.p.	B.p.	Found.	Calc.	Solvent used & remarks.
6-Methoxy-3 <i>n</i> -propyl-C	6-Hydroxy-3 <i>n</i> -propyl-C	C <sub>13</sub> H <sub>14</sub> O <sub>3</sub>	48-49°	—	C, 71.6% H, 6.5	71.55% 6.4	Petroleum ether
2- <i>iso</i> Valeryl-H	Hydroquinone & <i>iso</i> valeryl chloride by method I	—	114-15°	—	—	—	CCl <sub>4</sub> (cf. Klinger & Standke, <i>Ber.</i> , 1891, 24, 1345).
6-Hydroxy-3- <i>isopropyl</i> -C	2- <i>iso</i> Propyl-H & ethyl formate	C <sub>12</sub> H <sub>12</sub> O <sub>3</sub>	191-92°	—	C, 70.5 H, 5.8	70.6 5.9	Dil. EtOH, yield very poor.
6-Acetoxy-3- <i>isopropyl</i> -C	Acetylation of 6-hydroxy-3- <i>iso</i> -propyl-C	C <sub>14</sub> H <sub>14</sub> O <sub>4</sub>	88°	—	C, 68.3 H, 5.7	68.3 5.67	Dil. EtOH
2- <i>n</i> -Caproyl-H	(1) Hydroquinone & <i>n</i> -caproyl chloride by method I  (2) Demethylation of dimethyl ether of 2-caproyl-H by method III	C <sub>12</sub> H <sub>16</sub> O <sub>3</sub>	81-82°  81-82° (mixed)	—	C, 69.3 H, 7.72	69.23 7.7	Benzene.
6-Hydroxy- <i>n</i> -butyl-C	Hydroquinone & ethyl formate	C <sub>13</sub> H <sub>14</sub> O <sub>3</sub>	138°	—	C, 71.5 H, 6.6	71.55 6.4	Dil. EtOH
6-Methoxy-3- <i>n</i> -butyl-C	Methylation of 6-hydroxy-3- <i>n</i> -butyl-C	C <sub>14</sub> H <sub>16</sub> O <sub>3</sub>	63°	—	C, 72.4 H, 6.9	72.4 6.9	Petroleum ether (60-80°)
H-diheptate	H & heptoyl chloride heated on a water-bath for 6 hours	C <sub>20</sub> H <sub>30</sub> O <sub>4</sub>	57-48°	—	C, 71.9 H, 9.1	71.8 8.9	MeOH
2-Heptoyl-H	(1) H & heptoyl chloride by method I  (2) Fries' migration of dlheptate by method II  (3) Demethylation of dimethyl ether of 2-heptoyl-H by method III	C <sub>13</sub> H <sub>18</sub> O <sub>3</sub>	118°  118° (mixed)  118° (mixed)	—	C, 70.2 H, 8.0	70.26 8.1	Benzene.
6-Hydroxy-3- <i>n</i> -pentyl-C	2-Heptyol-H & ethyl formate	C <sub>14</sub> H <sub>16</sub> O <sub>3</sub>	146°	—	C, 72.3 H, 6.8	72.4 6.9	Dil. MeOH
6-Acetoxy-3- <i>n</i> -pentyl-C	Acetylation of 6-hydroxy-3- <i>n</i> -pentyl-C	C <sub>16</sub> H <sub>18</sub> O <sub>4</sub>	90-91°	—	C, 70.1 H, 6.7	70.0 6.6	Do
2-Lauroyl-H	Demethylation of its dimethyl ether (cf. Table I) by method III	C <sub>18</sub> H <sub>28</sub> O <sub>3</sub>	101°	—	C, 73.8 H, 9.5	74.0 9.6	Petroleum ether (60°-80°)
6-Hydroxy 3- <i>n</i> -decyl-H	2-Lauroyl-H & ethyl formate	C <sub>19</sub> H <sub>26</sub> O <sub>3</sub>	115°	—	C, 75.3 H, 8.7	75.5 8.6	Dil. EtOH

TABLE II (contd.)

Compounds.	Prepared from.	Mol formula.	M.p.	B.p.	Found.	Calc.	Solvent used and remarks.
2-Phenylacetyl-H	(1) H & phenylacetyl chloride by method I	C <sub>14</sub> H <sub>12</sub> O <sub>3</sub>	113°	—	C, 73.5% H, 5.3	73.7% 5.26	CCl <sub>4</sub>
	(2) Demethylation of dimethyl ether of 2-phenylacetyl-H by method III		113° (mixed)				
Diacetyl derivative of 2-phenylacetyl-H	Acetylation of 2-phenylacetyl-H	C <sub>18</sub> H <sub>16</sub> O <sub>6</sub>	141-142°	—	C, 69.1 H, 5.3	69.2 5.1	MeOH
6-Hydroxy-3-n-pentyl-C (6-hydroxy isoflavone)	2-Phenylacetyl-H & ethyl formate	C <sub>15</sub> H <sub>10</sub> O <sub>3</sub>	215-16°	—	C, 75.45 H, 4.1	75.6 4.2	Dil. MeOH
6-Methoxyisoflavone	Methylation of 6-hydroxyisoflavone	C <sub>16</sub> H <sub>12</sub> O <sub>3</sub>	170-71°	—	C, 76.1 H, 4.4	76.2 4.6	Do
6-Acetoxyisoflavone	Acetylation of 6-hydroxy isoflavone	C <sub>17</sub> H <sub>12</sub> O <sub>4</sub>	152°	—	C, 72.9 H, 4.4	72.82 4.2	Dil. MeOH
2-β-Phenylpropionyl-H	(1) Hydroquinone & hydrocinnamoyl chloride by method I	C <sub>15</sub> H <sub>14</sub> O <sub>3</sub>	119°	—	C, 74.3 H, 5.9	74.38 5.8	Do
	(2) Demethylation of dimethyl ether of 2-phenylpropionyl-H		119° (mixed)				
Dibenzoyl derivative of 2-β-phenylpropionyl-H	Benzoylation of 2-phenylpropionyl-H	C <sub>23</sub> H <sub>20</sub> O <sub>5</sub>	157°	—	C, 77.5 H, 4.9	77.3 4.9	"
6-Hydroxy-3-benzyl-C	2-Phenylpropionyl-H & ethyl formate	C <sub>16</sub> H <sub>12</sub> O <sub>3</sub>	226°	—	C, 76.3 H, 4.8	76.2 4.7	"
6-Methoxy-3-benzyl-C	Methylation of 6-hydroxy-3-benzyl-C.	C <sub>17</sub> H <sub>14</sub> O <sub>3</sub>	98-99°	—	C, 76.8 H, 5.3	76.7 5.26	Dilute ethyl alcohol
6-Acetoxy-3-benzyl-C.	Acetylation of 6-hydroxy-3-benzyl-C	C <sub>18</sub> H <sub>14</sub> O <sub>4</sub>	128°	—	C, 73.5 H, 4.8	73.48 4.75	"

## THE FORMATION OF THE IODO DERIVATIVES OF SUBSTITUTED AND BROMO-DISUBSTITUTED MALONAMIDES

By M. D. AVASARE, M. L. SHAH AND C. J. SHAH

Disubstituted malonamides have been iodinated and moniodo, diiodo and bromo-iodo derivatives obtained.

Naik and Shah (this *Journal*, 1930, 7, 239) tried to prepare iodo derivatives of substituted malonamides with iodine monochloride but they obtained only chloro derivatives. Several workers have obtained iodo compounds before in presence of various oxidising agents. We have iodinated substituted malonamides in presence of iodic acid as an oxidising agent and have obtained moniodo and diiodo derivatives from  $H_2C(CONHR)_2$  [where R is phenyl, *p*-tolyl, *o*-tolyl, 1:4.5-xylyl, 1:3:4-xylyl, *p*-bromophenyl, or hydrogen] and only moniodo derivatives have been obtained where R is benzyl or ethyl. In the case of malon-diphenylamide, iodine replaces the methylene hydrogen and not the hydrogen of the phenyl group, which is proved by the fact that iodine is readily reduced with potassium iodide and hydrochloric acid (Kurt Meyer, *Annalen*, 1911, 380, 212), whereas iodine attached to the phenyl group is not reduced by this method.

Bromomalon-di-*p*-bromoanilide, bromomalon-di-*p*-tolylamide and bromomalondi-benzylamide also react with iodine in presence of iodic acid and give rise to the corresponding bromiodo derivatives.

The iodo compounds so obtained are fairly stable and decompose only slowly on long standing. When compared with the corresponding chloro and bromo derivatives, which are quite stable, the instability is attributed to the larger atomic volume of iodine and consequently greater strain being so created in the molecule

### EXPERIMENTAL

The compound (2 g.) is dissolved in glacial acetic acid (60 to 90 c.c.) by heating under reflux on a sand-bath and is made to react with iodine (0.4 to 1.6 g.) in the presence of concentrated aqueous solution of iodic acid (0.2 to 0.7 g.). Iodine is slowly absorbed on shaking. When it is completely absorbed, the solution is filtered hot and the filtrate cooled when crystals of the resulting compounds are obtained. They are removed, washed with alcohol or benzene or in some cases with chloroform also and the melting point and solubility in organic solvents determined. They are readily soluble in alcohol, or benzene and in some cases in chloroform and sparingly soluble or insoluble in ether, chloroform and petroleum ether.

TABLE I

Iodo derivatives.	M. p.	Formula.	Iodine.	
			Found.	Calc.
1. Monoiodomalon-diphenylamide	Decomposes above 170° and melts at 198°	$C_{15}H_{13}O_2N_2I$	33.59%	33.42%
2. Diiodomalon-diphenylamide	130°	$C_{16}H_{12}O_2N_2I_2$	50.17	50.19
3. Monoiodomalon-di- <i>p</i> -tolylamide	Decomposes above 180° with liberation of iodine; 198°	$C_{17}H_{17}O_2N_2I$	30.77	31.13
4. Diiodomalon-di- <i>p</i> -tolylamide	136-37°	$C_{17}H_{16}O_2N_2I_2$	47.64	47.56
5. Monoiodomalon-di- <i>o</i> -tolylamide	Decomposes above 170°; 203°	$C_{17}H_{17}O_2N_2I$	31.33	31.13
6. Diiodomalon-di- <i>o</i> -tolylamide.	Decomposes above 165°; 187-88°	$C_{17}H_{16}O_2N_2I_2$	47.55	47.56
7. Monoiodomalon-di-xylylide (1:4:5)	Decomposes above 190°; 205°	$C_{18}H_{11}O_2N_2I$	29.27	29.13
8. Diiodomalon-di-xylylide (1:4:5)	Decomposes above 170°; 192-93°	$C_{19}H_{20}O_2N_2I_2$	45.12	45.2
9. Monoiodomalon-di-xylylide (1:3:4)	203-204°	$C_{19}H_{21}O_2N_2I$	28.98	29.13
10. Diiodomalon-di-xylylide (1:3:4)	108-109°	$C_{19}H_{20}O_2N_2I_2$	45.14	45.2
11. Monoiodomalon-di- <i>p</i> -bromoanilide	Decomposes above 190°; 218°	$C_{16}H_{11}O_2N_2BrI$	23.56	23.6
12. Diiodomalon-di- <i>p</i> -bromoanilide	Decomposes above 160°; 205°	$C_{16}H_{10}O_2N_2Br_2I_2$	38.21	38.24
13. Monoiodomalonamide	Decomposes above 190°; 201-2°	$C_3H_5O_2N_2I$	55.88	55.71
14. Diiodomaloamide	Decomposes above 160°; 198-99°	$C_3H_4O_2N_2I_2$	71.61	71.74
15. Monoiodomalon-monophenylamide	176°	$C_9H_9O_2N_2I$	41.84	41.78
16. Diiodomalon-mono phenylamide	140°	$C_9H_8O_2N_2I_2$	58.99	59.06
17. Monoiodomalon-dibenzylamide	171°	$C_{17}H_{17}O_2N_2I$	31.3	31.13
18. Monoiodomalon-diethylamide	168°	$C_7H_{13}O_2N_2I$	44.42	44.72
19. Bromoiodomalon-di- <i>p</i> -bromoanilide	Decomposes above 155°; 171°	$C_{16}H_{10}O_2N_2Br_3I$	20.57	20.58
20. Bromoiodomalon-di- <i>p</i> -tolylamide	138°	$C_{17}H_{16}O_2N_2BrI$	26.02	26.08
21. Bromoiodomalon-dibenzylamide	109°	$C_{17}H_{16}O_2N_2BrI$	26.1	26.08

## STUDIES IN CO-SOLVENCY. PART IV. SOLUBILITY OF STEARATES OF LITHIUM, SODIUM AND POTASSIUM IN GLYCOLIC MIXTURES\*

BY SHREEPATI RAO AND SANTI R. PALIT

Measurements have been made of the solubility of stearates of lithium, sodium and potassium at 35° in binary solvent mixtures one component of which is propylene or diethylene glycol and the other is chloroform, ethylene dichloride or benzene. A few measurements have been recorded using alcohols in place of glycols in the above binary mixtures.

It is observed that the glycolic mixtures improve to a great extent the solvent power of the individual solvents and the results are found to be in agreement with previous observations and the already postulated mechanism.

It has been already shown in previous papers (Palit, this *Journal*, 1942, **19**, 271 ; *J. Amer. Chem. Soc.*, 1947, **69**, 3120 ; Palit and McBain, *J. Amer. Oil Chem. Soc.*, 1947, **24**, 190) of this series that soaps of alkali metals and heavy metals dissolve strongly in mixtures of a glycol (here called G-solvent for brevity) and a hydrocarbon-dissolving solvent (called H-solvent) such as hydrocarbons, chlorinated hydrocarbons, higher alcohols and the like. This co-solvency is attributed to the existence of polar-nonpolar combination in the soap molecule, the polar oxygen in the  $\text{-COO}^-$  group being solvated and thus dissolved through hydrogen bonds with the glycols, and the hydrocarbon portion being dissolved by the other co-solvent in the G-H mixture.

So far no work has been published with the stearates of lithium and potassium and the present paper presents the results on these substances. Data on lithium soap are of special interest as they have been lately used to a larger extent in the manufacture of lubricating grease to impart to it special properties. New data for sodium stearates have also been included for comparison and also because the previous work was done with rather impure samples of stearic acids, whereas a very pure sample of stearic acid has been used in this investigation.

### EXPERIMENTAL

Stearic acid was obtained by the following method of purification. Commercial triple pressed stearic acid was converted into its lead soap and the liquid acids were separated from the solid acids by fractional crystallisation in alcohol (Hilditch, "The Chemistry of Fats and Oils," 1947, p. 468). The solid acids were first converted into the ethyl esters which were fractionated in vacuum twice and were hydrolysed to get back the stearic acid. The stearic acid was next converted into the methyl ester and fractionated three times under vacuum and a constant boiling fraction of methyl stearate was isolated; this fraction was saponified to get stearic acid which was observed to have a melting point of 68.5°. It was then dissolved in alcohol and boiled with active animal charcoal and the solution was filtered hot and allowed to crystallise. The crystals of stearic acids were recrystallised twice more from alcohol and were used in the present experiments.

\* Contribution No. 11 from the Department of Physical Chemistry, Indian Association for the Cultivation of Science, Calcutta.

TABLE I  
Solubility of soaps at 35° in co-solvent mixtures (g./100 g. solvents)  
Volume per cent glycol (volume per cent alcohol where no glycol is present)

Composition of solvent.	0.	10.	20.	30.	40.	50.	60.	70.	80.	90.	100.	Curve No
					(a) Lithium stearate							
Propylene glycol-chloroform	0.00	—	0.58	—	0.56	—	0.24	—	0.068	—	0.04	1
Propylene glycol-ethylene dichloride	0.00	0.00	0.03	0.06	0.09	—	0.18	—	0.19	—	0.04	2
Propylene glycol-n-butyl alcohol	0.03	0.101	0.15	0.16	0.17	—	0.16	—	0.12	—	0.04	3
					(b) Sodium stearate							
Propylene glycol-chloroform	0.00	—	4.25	—	7.55	7.90	6.79	—	3.85	—	1.68	14
Propylene glycol-ethylene dichloride	0.00	—	1.70	—	3.27	3.98	3.87	—	2.96	—	1.68	15
Diethylene glycol-ethylene dichloride	0.00	—	1.32	—	2.07	2.28	2.36	—	2.24	—	1.04	16
Diethylene glycol-chloroform	0.00	—	3.98	—	4.35	3.01	3.34	—	1.80	—	1.04	17
					(c) Potassium stearate.							
Propylene glycol-chloroform	0.01	4.83	9.17	13.70	16.40	—	18.16	—	15.57	—	6.35	4
Propylene glycol-ethylene dichloride	0.00	3.22	6.97	9.33	11.92	—	14.50	—	13.54	—	6.35	5
n-Butyl alcohol-benzene	0.00	0.04	0.14	0.26	0.37	—	0.50	—	0.52	—	0.47	6
n-Butyl alcohol-chloroform	0.01	0.05	0.10	0.23	0.34	—	0.43	—	0.51	—	0.47	7
Methanol-chloroform	0.01	0.44	1.17	1.87	2.41	—	3.19	—	3.98	—	4.58	8
Ethyl alcohol-chloroform	0.01	0.23	0.75	1.19	1.46	—	1.66	—	1.55	—	1.42	9
Propylene glycol-benzene	0.00	8.28	14.14	18.55	21.08	—	25.60	—	20.52	—	6.35	10
Diethylene glycol-benzene	0.00	9.75	15.83	21.05	23.51	—	24.24	—	18.24	—	6.54	11
Diethylene glycol-chloroform	0.01	6.92	12.90	17.10	19.92	—	22.04	—	16.34	—	6.54	12
Diethylene glycol-ethylene dichloride	0.00	—	7.93	—	13.23	14.60	15.40	—	12.86	—	6.54	13

Stearates of sodium and potassium were obtained by the usual method of neutralising stearic acid in aqueous alcohol with the requisite amount of caustic solution free from carbonate. Lithium stearate was prepared by precipitating warm lithium chloride in slight excess with warm sodium stearate solution and washing the precipitated lithium stearate repeatedly with warm water until free from chloride. The stearates were dried at 110° for 3 hours and stored in vacuum desiccators.

Solubility measurements were done by the method described before (Palit, *J. Amer. Chem. Soc.*, *loc. cit.*). The analysis of the saturated solution was carried out by the direct titration method (Palit, *Oil & Soap*, 1946, **23**, 58; *Ind. Eng. Chem. Anal. Ed.*, 1946, **18**, 246) with standard perchloric acid in ethylene glycol-isopropyl alcohol mixture (1:1) using thymol blue as an indicator.  $N/32$  normal acid was used for measurements with lithium stearate and  $N/10$  normal acid was used for measurements with sodium and potassium soaps. Even with such a dilute solution of perchloric acid the end-point could be determined with great accuracy, the colour of the thymol blue changing sharply from yellow to red at the equivalence point.

The results are presented in Table I and graphically represented in Fig. 1, 2 and 3. For convenience of reference all co-solvency curves (seventeen in all) have been drawn as in previous publications with pure *i. e.*, 100% glycolic solvent on the right hand extreme of the diagram. It may be noted that our present results with sodium stearate are fairly consistent with our previous data (Palit, *this Journal*, *loc. cit.*) if allowance is made for a temperature difference of 10°. On comparing curves 1, 4 and 14 against those of stearates of heavy metals (Pb, Ca, Mg and Zn) in the same solvent mixture *e. g.*, propylene glycol-chloroform (Palit and McBain, *loc. cit.*) it is observed that Li, Na and K stearates show maximum co-solvency at a higher proportion of the glycolic solvent which points to the fact that the alkali metal soaps are more polar than the heavy metal soaps.

#### DISCUSSION

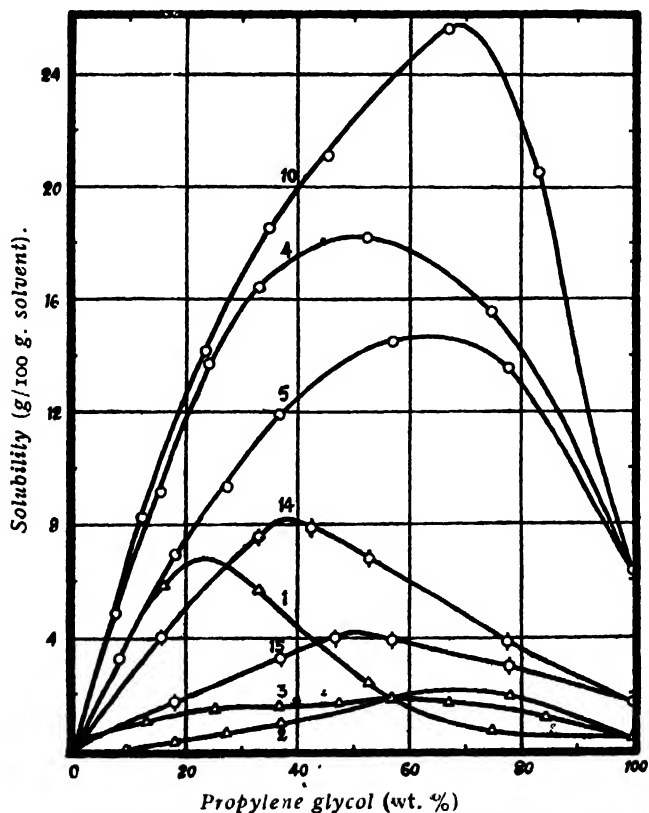
*Comparison of Li, Na and K.*—It will be observed from Fig. 1 where we have collected the co-solvency curves for Li, Na and K in the same solvent mixtures, propylene glycol-ethylene chloride and also propylene glycol-chloroform, that all the systems show a striking degree of co-solvency, the solubility in the glycol being increased over three times by adding a non-solvent, *e. g.*, chloroform or ethylene dichloride. The solubility in general varies in the order: potassium  $\gg$  sodium  $>$  lithium. It is remarkable that though the lithium soap is extremely insoluble, it unmistakably shows the phenomenon of co-solvency in glycolic mixtures even at such low solubility.

In Fig. 1 we have also included the curve for the solubility of potassium stearate in propylene glycol-benzene mixture (curve 10) which is found to run at the top of all other curves. The measurement with this immiscible liquid pair has been made possible by the fact that the addition of potassium stearate brings about a complete miscibility. The same is also true of diethylene glycol-benzene system with potassium stearate the curve (No. 11) for which is presented in Fig. 2. That benzene is a better co-solvent than the chlorinated hydrocarbons has also been previously observed (Palit,

*J. Amer. Chem. Soc., loc. cit.*) in the case of sodium oleate and this is now found to be true for potassium stearate.

**Alcohols as Glycolic Solvents.**—In order to test how far the glycolic property is possessed by monohydric alcohols, experiments were conducted to determine the solubility of potassium stearate in chloroform-alcohol mixtures. Potassium stearate was chosen for study as it was felt that the solubility of the other two soaps was too small to definitely reveal such co-solvency, if it existed to only a small degree. Of the three alcohols tested (methyl, ethyl and *n*-butyl) it will be observed from Fig. 3 that methyl alcohol (curve No. 8) shows a practically linear curve, whereas there is a slight convexity in the case of ethyl alcohol (No. 9); butyl alcohol (No. 7), however, shows a very small though definite maximum. This shows that alcohols have very poor co-dissolving power for alkali metal stearates and this co-dissolving power seems to increase with higher alcohols. That this weak co-dissolving power of butyl alcohol is real is further shown by the fact that when chloroform is substituted by benzene in the above study there is observed, as would be seen from Fig. 2 (No. 6), a stronger co-

FIG. 1  
Co-solvency curves

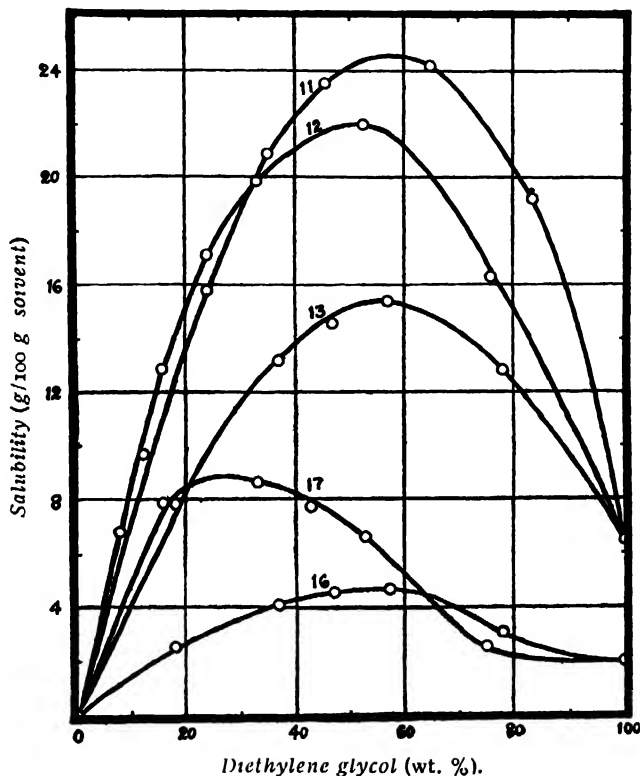


Lithium stearate in propylene glycol-chloroform (1), -ethylene dichloride (2), -benzene (3), (ordinates of 1, 2 and 3 have been 10 times magnified); sodium stearate in propylene glycol-chloroform (14), -ethylene dichloride (15); potassium stearate in propylene glycol-benzene (10), -chloroform (4) and -ethylene dichloride (5).



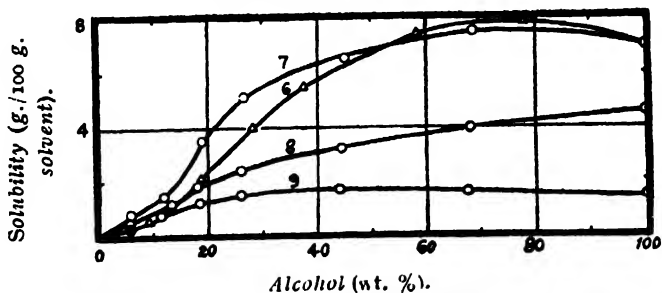
solveny in conformity with the already established fact that benzene is a stronger H-cosolvent than chloroform. It will be further observed that the co-solvency maximum for ethyl alcohol occurs much towards the left of the maximum for butyl alcohol con-

FIG. 2  
*Co-solvency curves*



Potassium stearate in diethylene glycol-benzene (11), -chloroform (12) and -ethylene dichloride (13) ; sodium stearate in diethylene glycol-chloroform (17) ethylene dichloride (16). (The ordinates of curves 16 and 17 have doubly magnified).

FIG. 3  
*Solubility in mixed solvents*



Potassium stearate in  $\text{CHCl}_3$ -MeOH (8), chloroform ethyl alcohol (9), chloroform-*n* butyl alcohol (7) and benzene-*n*-butyl alcohol (6). (The ordinates of curves 6 and 7 have been magnified 15 times for convenience in representation).

sistent with the fact that ethyl alcohol contains less proportion of hydrocarbon than butyl alcohol.

We had previously observed (Palit, *loc. cit.*) that among aliphatic alcohols methyl alcohol was the best solvent for sodium oleate. Here, for potassium stearate, we observe the same behaviour.

*Comparison of Chloroform and Ethylene Dichloride.*—We have five pairs of curves (1 & 2, 4 & 5, 12 & 13, 14 & 15, 16 & 17) for comparison between chloroform and ethylene dichloride. All the five pairs show the following common features. Firstly, the co-solvency maximum for ethylene dichloride always occurs on the right of the corresponding maximum with chloroform. This agrees with our previous findings with sodium stearate and sodium oleate. In three cases the difference is only of a few per cent, but in the remaining two cases the maxima are widely separated; for example, with lithium stearate the maxima are at 29 and 72 volume per cent propylene glycol for chloroform and ethylene dichloride respectively, and for sodium stearate the corresponding figures are 33 and 60 volume per cent using diethylene glycol as the glycolic co-solvent. It is noteworthy that for sodium stearate, though the maxima are only separated by only 5 volume per cent units with propylene glycol, the separation becomes widened to over 25 units by passing to diethylene glycol.

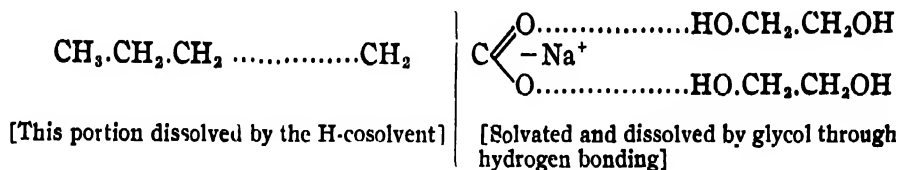
Secondly, in all the five pairs it is observed that the maximum solubility reached with chloroform under otherwise identical conditions is always higher than that obtainable with ethylene dichloride. This also agrees with our previous observations with sodium oleate and stearate, and may be interpreted as showing that chloroform is a better hydrocarbon-dissolving solvent than ethylene dichloride.

*Comparison of the two Glycols.*—In this paper we have not presented any data for ethylene glycol as the H-co-solvents used herein *i. e.*, chloroform-ethylene dichloride, etc., are too immiscible with it to be amenable to such co-solvency measurements. From all our previous and also present data with sodium stearate and oleate, we found propylene glycol (P. G.) a much better solvent than diethylene glycol (D. G.) for the pure soap. In potassium stearate we have met the reverse behaviour. Weight per weight, D. G. is found to be a slightly better solvent than P. G. for K-stearate. However, the co-solvency curves for D. G. with both chloroform and ethylene dichloride run higher above the corresponding curves for P. G. in agreement with our previous work. P. G. has also been found to require less H-solvent than D. G. to produce the maximum solubility which is expected from the already established fact that D. G. is a stronger glycolic solvent than P. G. (*vide*, Fig. 6, Palit, *J. Amer. Chem. Soc.*, *loc. cit.*).

*Stearates and Oleates compared.*—On comparing the present data for sodium stearate with the previously published data on sodium oleate it is observed that as expected the stearates are much less soluble than the oleates. Further, for sodium stearate the co-solvency maximum always occurs more towards the left hand side (*i. e.*, glycol-poor region) than the corresponding point for the sodium oleate. This is easily understandable as stearate being more hydrocarbon-like and less soluble in hydrocarbons requires a higher proportion of H-solvent to bring about the maximum possible solubility.

*Height and Position of the Co-solvency Maxima.*—The general trends of these two

features of the maxima are in general agreement with what would be expected if we accept the picture that the co-solvency arises from the fact that the hydrocarbon portion is dissolved by the H-cosolvent and the  $-\text{COO}^-$  portion is dissolved by the G-cosolvent as previously postulated and as shown below.



We are, however, as yet far from deducing any quantitative guide as to an approximate idea of these two features. For example, if we are confronted with the question of giving an approximate idea of the height and position of the co-solvency maximum in an hitherto uninvestigated soap system, say, sodium laurate in diethylene glycol-chloroform mixture, it becomes difficult to make any quantitative prediction. Our already observed findings make us bold to presage that the position of the maximum will be towards the right side of that of sodium stearate or myristate under identical conditions, and also towards the left side of the maxima for the same system using ethylene dichloride in place of chloroform, or propylene glycol in place of diethylene glycol. We can further say that the per cent increase of the maxima over the mean solubility at that composition will be less than that of its higher homologues.

The authors desire to express their thanks to Sri Ranajit Sengupta for carrying out a major part of the work for the purification of the stearic acid used in this investigation.

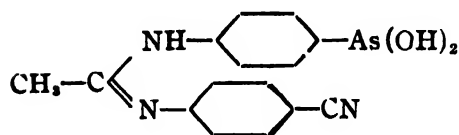
# ON ORGANO-ARSENICAL COMPOUNDS. PART V

By B. PATHAK AND T. N. GHOSH

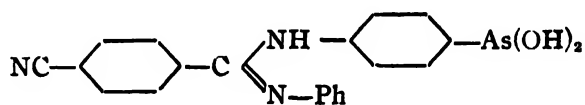
Some diamidine derivatives of the types (III and IV), containing arsenious acid group, have been synthesised

It has been shown by Ashley *et al.* (*J. Chem. Soc.*, 1942, 103) that the aromatic symmetrical diamidines have outstanding antiparasitic properties against protozoa. It is not known whether such activity depends specifically on the amidine group which may function by assisting adsorption, through the resonance of its ion, or by interfering with a similarly constituted metabolite in the parasite (cf. Albert *et al.*, *ibid.*, 1947, 1452). It is also known that certain arsenic derivatives have a beneficial effect on patients suffering from various forms of trypanosomiasis. Whether the presence of both arsenic and amidino groups in one molecule will stimulate, or suppress, such action has still to be determined. With this object in view, it has been considered desirable to synthesise some diamidines containing arsenious acid group.

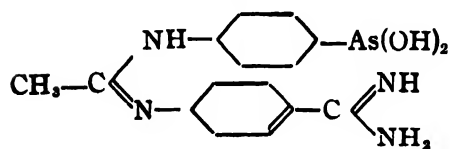
In parts III and IV (Pathak and Ghosh, this *Journal*, 1949, 26, 254, 293) of this series of papers, it has been shown that N-alkylated amidines containing arsenious acid group are obtained by reacting acetanilide or its derivatives with *p*-arsanilic acid in presence of phosphorus oxychloride. *p*-Cyanoacetanilide has now been reacted with *p*-arsanilic acid in presence of phosphorus oxychloride to yield a mixture of the acetamidine derivative (I) and a compound (m.p. 182-84°) containing chlorine but no arsenic, the constitution of which could not be definitely ascertained. Similarly, the condensation of *p*-cyanobenzanilide with *p*-arsanilic acid in presence of phosphorus oxychloride has furnished a mixture of the benzamidine derivative (II) and a non-arsenical chloro compound (m.p. 190-92°) of undetermined constitution.



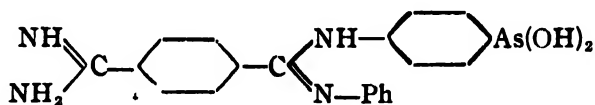
(I)



(II)



(III)



(IV)

Attempts were made to prepare the imino-ether hydrochlorides of the above cyano compounds (I and II), containing strong basic groups, in ether, benzene or chloroform but in each case passing of dry hydrogen chloride caused immediate formation and precipitation of the cyano hydrochlorides. The problem has been, however, solved by

the discovery that nitrobenzene (cf. Ashley *et al.*, *loc. cit.*; U. S. P., 2,204, 983; B. P. 510,097) is an excellent solvent for these cyano hydrochlorides and also for the resulting imino-ether hydrochlorides, the latter having been almost quantitatively precipitated by the addition of ether. The imino-ether hydrochlorides, thus obtained, have easily furnished the arsenious acid derivatives (III and IV), both of which contain an unsubstituted and a substituted amidino group. These compounds (III and IV) readily respond to the specific colour reaction as discovered by Fuller (*Nature*, 1944, 154, 773) for unsubstituted aromatic amidines.

### EXPERIMENTAL

(Phenyl-4-cyano) (phenyl-4-arsenious acid)-acetamidine (I).—An intimate mixture of *p*-cyanoacetanilide (16 g., prepared according to the method of Bogoslovskii, *J. Gen. Chem.*, U. S. S. R., 1938, 1, 1784) and *p*-arsanilic acid (21.7 g.) was gradually added to phosphorus oxychloride (90 c.c.) and the mixture was then heated in an oil-bath at 125°–130° for 5 hours. Next day, the reaction mixture was poured into crushed ice, when on stirring a pasty mass was obtained. The supernatant liquid was decanted and basified with ammonium hydroxide, when a solid was precipitated. This solid was mixed with the above pasty mass and the total quantity was then triturated with 5% caustic soda solution and finally filtered.

The alkaline filtrate was treated with charcoal, filtered and acidified with dilute hydrochloric acid. The acidic solution, when basified with ammonium hydroxide, precipitated a cream-colored solid which is soluble in alcohol and in acetic acid. It could not be induced to crystallise from any of these solvents and was therefore purified by dissolving in 5% caustic soda solution, acidification with dilute hydrochloric acid and finally treatment with excess of ammonium hydroxide. The solid (7 g.), when dried *in vacuo*, begins to shrink and soften at 200° and melts at 210° to a viscous mass. (Found: As, 21.45; N, 11.9.  $C_{13}H_{14}O_2N_3As$  requires As, 21.84; N, 12.24 per cent). It is readily soluble in dilute hydrochloric acid and in dilute alkali but insoluble in aqueous ammonia or bicarbonate. Its acetic acid solution readily decolorises iodine solution. From its solution in 10% caustic soda solution it is precipitated as such when saturated with sodium chloride. The same compound (I) has been obtained by reacting *p*-aminophenylarsenoxide with *p*-cyanoacetanilide in presence of phosphorus oxychloride under identical conditions, which shows conclusively that (I) is an arsenious acid derivative and not an arsonic acid.

The alkali-insoluble solid was crystallised twice from alcohol in cream-colored needles (6.5 g.), m.p. 182–84°. The constitution of this compound, which contains chlorine but no arsenic, could not be definitely ascertained.

(Phenyl)-(phenyl-4-arsenious acid)-*p*-cyanobenzamidine (II). — *p*-Cyanobenzanilide has been prepared by reacting *p*-cyanobenzoyl chloride (Ashley *et al.*, *loc. cit.*) with aniline. It melts at 178–79° (cf. Fischer and Wolter, *J. prakt. Chem.*, 1909, ii, 80, 102).

The method of condensation of *p*-cyanobenzanilide with *p*-arsanilic acid and that of isolation of the reaction products were the same as described above. The light yellow solid (compound II), which is readily soluble in dilute hydrochloric acid and in dilute alkali but insoluble in aqueous ammonia or bicarbonate, shrinks at 220° and melts

to a viscous mass at 270°. (Found: As, 17.87.  $C_{10}H_{11}O_2N_2As$  requires As, 18.49 per cent).

The alkali-insoluble solid was found to be a crude hydrochloride. The free base was obtained by dissolving the hydrochloride in boiling water and treating the solution with alkali, when a brownish solid was precipitated. It was crystallised from alcohol in cream-colored rectangular plates, m.p. 190-92°. The constitution of this compound, which contains chlorine but no arsenic and furnishes, when treated with alcoholic hydrochloric acid, a hydrochloride (m.p. 320-22°), could not be definitely ascertained.

(*Phenyl-4-amidino*)-(phenyl-4-arsenious acid)-acetamidine (III).—A solution of the compound (I, 5 g.) in dry nitrobenzene (100 c.c.) was saturated at 0° with dry hydrochloric acid gas and the resulting solution was then kept in a closed vessel in the refrigerator for 6 days with occasional shaking. The imino-ether hydrochloride was then precipitated by addition of dry ether (400 c.c.), filtered, washed with dry ether and dried in a vacuum desiccator. It was treated with 15% alcoholic ammonia (50 c.c.) and the mixture was heated in a closed vessel at 110°-115° for 5 hours. After cooling overnight, the almost colorless precipitate, which was found to consist mainly of ammonium chloride, was filtered and the filtrate distilled under reduced pressure to remove as much of alcohol as possible. The residue was treated with ammonium hydroxide, when a solid was obtained. It could not be induced to crystallise from alcohol or any other organic solvent and was purified by solution in cold dilute alkali, acidification under cooling with dilute hydrochloric acid and finally treatment with excess of ammonium hydroxide. The brownish solid (2.8 g.), which was dried *in vacuo*, softens at 240° and melts at 250° to a viscous mass. (Found: As, 20.12; N, 15.18.  $C_{15}H_{17}O_2N_4As$  requires As, 20.81; N, 15.56 per cent).

(*Phenyl*)-(phenyl-4-arsenious acid)-p-amidinobenzamidine (IV).—The method of preparation was the same as described above. The light yellow solid melts to a viscous mass at 302°. (Found: N, 12.94.  $C_{20}H_{19}O_2N_4As$  requires N, 13.27 per cent).

(4:4'-*Diamidinodiphenyl*)-(4:4'-arsenophenyl)-acetamidine (V).—A solution of the compound (III, 1 g.) in the requisite quantity of 5% hydrochloric acid was reduced by adding, with stirring, 35% hypophosphorous acid (8 c.c.) and 1 c.c. of 1% aqueous solution of potassium iodide. Soon the solution became turbid and a precipitate was formed. The reaction mixture, after being occasionally stirred at room temperature for about 3 hours, was triturated with excess of 10% cold caustic soda solution. The resulting light brown solid was filtered, again triturated with 10% caustic soda solution, filtered, washed thoroughly with water till free from chloride and dried *in vacuo*. It melts at 256-58° (decomp.). (Found: As, 22.3.  $C_{18}H_{19}N_5As_2$  requires As, 22.9 per cent).

## ON THE BROMINATION OF CRESOL

By N. RAY

A process of inhibiting the overbromination of the cresols has been worked out, which is found to be independent of temperature as well as of the concentration of bromine or acid added. A mechanism of the overbromination and of its inhibition has been explained. An easy and accurate method of estimating cresols by bromination has also been suggested.

Cresol is a mixture of its three isomers which are present roughly in the proportion  $o : m : p = 35 : 40 : 25$  (Chapin, *J. Biol. Chem.*, 1921, **47**, 309). Of these the *m*-cresol (Beukema-Goudsmit, *Pharm. Weekblad*, 1934, **71**, 380) can easily be estimated by the koppeschaar's method of bromination (*Z. anal. Chem.*, 1876, **15**, 233). Auwers and Anselmino (*Ber.*, 1899, **32**, 3587) showed that liquid bromine may cause substitution in the *o*- and *p*-methyl group or even lead to the complete replacement of the *p*-methyl group. Phenol-cresol mixture and lysol (Järvinen, *Z. anal. Chem.*, 1927, **71**, 108; N. Ray, unpublished data) have been estimated to a considerable degree of accuracy assuming a more or less arbitrary value of cresol. No general procedure, however, for estimating cresol by this method is known upto now. Ruderman (*Ind. Eng. Chem. Anal. Ed.*, 1946, **18**, 753) found that a number of factors, such as period of bromination, the acid concentration and the temperature, influenced the potential reactivity of phenols, which may lead to overbromination under certain conditions. The effect of concentration of reactants, however, does not appear to have been investigated so far. In view of the observation (Ray, *Proc. J. Inst. Chem.*, 1944, **16**, 76) that sulphanilamide is liable to be overbrominated in dilute solutions but undergoes quantitative bromination in the nucleus only in a solution saturated with an alkali halide, it appears that the overbromination of cresol in dilute solutions may also be a similar phenomenon. A study of the effect of concentration of the reactants on the bromination of cresol is of interest, and the results of the work carried so far are presented in this paper.

### EXPERIMENTAL

One mole of cresol would theoretically require 4.8 moles of bromine for bromination in the nucleus. Thus 1 c.c. of 0.1 *N*- $\text{Na}_2\text{S}_2\text{O}_3$  solution would be equivalent to 0.00225 g. of cresol. Relatively dilute solutions of the reactants were taken for the study of the degree of overbromination at the room temperature of 30°-33°. But in order to show the effect of high concentration of the reactants on the course of bromination either concentrations of the reactants were so adjusted that the solvent was completely or nearly saturated, or the solvent (water) of the reactants in a dilute solution was saturated by the addition of a suitable alkali halide before adding to the reactants the acid for evolution of bromine.

**Method.**—An aqueous solution of cresol (2 c.c.) containing 6-15 mg. was reacted with bromine from a mixture of potassium bromide and bromate solution to which 10 c.c. of 1:1 hydrochloric acid were added. This reaction was allowed for 10 minutes. The reac-

tion with potassium iodide for liberation of iodine to be titrated against  $N/10$ -sodium thiosulphate was also allowed 10 minutes. The reactions were all carried out in the dark.

For dilute solution of the reactants 3 c.c. of 25% potassium bromide and 10 c.c. of 0.1*N*- potassium bromate solution were accurately measured by a pipette, and the total volume of the mixture was maintained at about 50 c.c. by the addition of water, if necessary.

TABLE I

*Overbromination of cresol in dilute solutions.*

Cresol taken.	B r o m i n e				Cresol found	Over- bromination.
	Added	Consumed.	Theoretically required.	Bromine equiv. corres- ponding to the potential reactivity of cresol.		
6.012 mg.	80 mg.	24.39 mg.	21.38 mg.	5.477	6.86 mg.	14.1%
6.012	80	24.61	21.38	5.525	6.92	15.1
6.274	80	26.07	22.31	5.698	7.33	16.9
6.274	80	27.92	22.31	6.006	7.85	25.1
6.274	80	26.68	22.31	5.900	7.54	19.6
6.274	80	27.09	22.31	5.828	7.62	21.1
9.412	80	41.74	34.35	5.985	11.74	24.7
12.548	80	49.87	44.61	5.349	14.02	11.8
15.685	80	59.94	55.77	5.158	16.86	7.8

## DISCUSSION

It was found for a cresol solution containing 6.0 mg. of cresol in 50 c.c., 4 times the theoretical quantity (22.0 mg.) of bromine, under the condition of the experiment, would overbrominate the cresol to an extent which gave (Table I) 14 to 25% too high value for the cresol. When the quantity of cresol was increased, while keeping other reactants and the volume of the mixture the same, that is, with the decrease of the ratio of the amount of added bromine to that consumed, the degree of overbromination also showed a decrease, pointing to the observation of Francis and Hill (*J. Amer. Chem. Soc.*, 1941, **63**, 357) that with a very slight excess of bromine the overbromination might be avoided. Table I will show that 1.45 times the required bromine i.e. an excess of 24 mg. of bromine over that theoretically required gave a cresol value which was only 7.8% too high. Remembering that the nuclear substitutions have the velocity constant (Francis, Hill and Johnston, *J. Amer. Chem. Soc.*, 1925, **47**, 2213, 2228) of the order of  $10^6$ , in which case no interval is necessary for bromination after the appearance of free bromine, it might be assumed here that some bromine went over to the methyl group (Sprung, *Ind. Eng. Chem. Anal. Ed.*, 1941, **13**, 35) or to the



methylene quinone (cf. Ruderman, *loc. cit.*) that might have been formed, where a period of 10 minutes was given for the bromination.

On the other hand, when the volume of the solution containing the cresol was so adjusted that the added reactants, potassium bromide and bromate, completely or nearly saturated the solution, the bromination was found to be quantitative (Table II) for the nuclear substitution according to the theory.

TABLE II

*Inhibition of overbromination.*

Cresol taken.	KBr taken.	KBrO <sub>3</sub> taken.	HCl taken	Bromine from the bromide-bromate mixture.	Vol. of the reactant mixture.	Saturation with.	Cresol found.	Error.
9.412 mg.	750 mg.	27.83 mg.	10 c c	80 mg.	25 c.c	—	9.426 mg.	+0.15%
6.274	750	27.83	10	80	20	—	6.322	+0.77
9.412	750	56.0	10	160.9	16	KCl-KBr	9.306	-1.10
9.412	2000	56.0	5	160.9	8	KBr	9.068	-3.70
9.412	750	27.83	10	80	25	NaCl	9.128	-3.02

The saturation of the dilute solution by addition of sodium chloride before adding the hydrochloric acid to the mixture of the reactants was also found to facilitate nuclear bromination only. The above observation points to the influence of solvent (water) on the extranuclear bromination of cresol. The presence of more water than is necessary for saturation (Table I) leads to substitution in the methyl group.

Alkali salts are known to be highly solvated in aqueous solution. Their presence in a high concentration would remove much of the free water and would thereby depress the solubility of bromine. Further, the increased ionic concentration in the solution would diminish the activity coefficient of bromine (Hammett, "Physical Organic Chemistry", New York, 1940, p. 90). Both these effects would tend to decrease the velocity of reaction between bromine and cresol molecules, both in the nucleus and in the side-chain. But as the velocity constant for the nuclear bromination is very high compared to that in the side-chain (Francis, Hill and Johnston, *loc. cit.*), it may be suggested that due to the presence of salts, the reaction rates are reduced to such an extent that only the faster reaction becomes effective and the slower one does not proceed to any appreciable extent during the time allowed for the reaction to proceed. It is assumed that in the absence of the salt the nuclear substitution becomes practically instantaneous and that in the side chain is also sufficiently fast to be appreciable within the given time.

The extranuclear bromination of cresols may be considered in the light of the theory of resonance also. In the bromination of cresols it may be supposed that the directing influence of the hydroxyl group due to resonance would predominate over the inductive effect of the methyl group, and nuclear substitution would take place in the *o*- and *p*-positions to the -OH group. This would also hinder any tendency of

substitution of bromine in position *meta* to the -OH group (cf. Sprung, *loc. cit.*). While the resonance in the *m*-cresol is completely stopped by the nuclear bromination, it is not so in the case of *o*- and *p*-cresols. The resonance effect (Pauling, *J. Amer. Chem. Soc.*, 1936, **58**, 94; 1935, **57**, 2705; 1937, **59**, 1223) may be considered to result in the substitution of bromine in the methyl group, presumably through the formation of ionic intermediates, where the methyl carbon would be linked to the nuclear carbon through a double bond. Such a reaction would be facilitated in a hydroxylic solvent (cf. Buckles, *J. Amer. Chem. Soc.*, 1949, **71**, 1157), and thus will explain the effect of high concentration of alkali salts such as bromide or chloride which removes much of the available solvent and is found to inhibit this type of reaction (Terry and Eichelberger, *J. Amer. Chem. Soc.*, 1925, **47**, 1067).

It will thus be evident from Table II that even a great excess of bromine could not induce bromination at the side-chain, the reaction being in presence of a high concentration of alkali halides. The temperature of the reactions of bromination was 30°-33° which might well be considered appreciably high (cf. Ruderman, Sprung, *loc. cit.*). The bromide-bromate mixture, the acid concentration, the period of reaction and the total volume of the reactant mixture were varied widely, but due to the saturation of the solvent, the bromination became quantitatively nuclear. Further evidence is necessary for elucidating the actual mechanism of the bromination.

The process of bromination of cresol in an acid solution, saturated with the alkali salt of the same acid, such as hydrochloric acid, would provide for a quick and easy method of estimating the cresols accurately with reproducible results.

In conclusion, the author wishes to express his sincere thanks to Dr. U. P. Basu, D.Sc., F.N.I, for his encouragement in the work.

BENGAL IMMUNITY RESEARCH LABORATORY,  
CALCUTTA.

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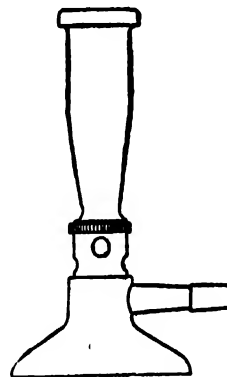
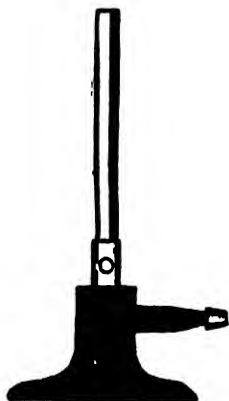
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